

A class of energy based ensembles in Tsallis statistics

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Abstract

A comprehensive investigation is carried out on the class of energy based ensembles. The eight ensembles are divided into two main classes. In the isothermal class of ensembles the individual members are at the same temperature. A unified framework is evolved to describe the four isothermal ensembles. Such a description is provided both in the second and the third constraint formalisms. The isothermal-isobaric, grandcanonical and the generalized ensembles are illustrated through a study of the classical nonrelativistic and the extreme relativistic ideal gas models. In the adiabatic class of ensembles the individual members of the ensemble have the same value of the heat function and a unified formulation to described all the four ensembles is given. The nonrelativistic and the extreme relativistic ideal gases are studied in the isoenthalpic-isobaric ensemble, the adiabatic ensemble with number fluctuations, and, the adiabatic ensemble with number and particle fluctuations.

PACS Number(s): 05.20.-y, 05.70

Keywords: Nonextensivity; ensemble theory; isothermal class; adiabatic class.

I Introduction

Boltzmann-Gibbs extensive statistical mechanics was generalized by Tsallis through the use of a deformed logarithm function in the entropic expression [1]. The functional form of the entropy defined in terms of the deformed logarithm is

$$S_q = -k \sum_i \mathbf{p}_i^q \ln_q \mathbf{p}_i, \quad q \in \mathbb{R}_+, \quad (1.1)$$

where k is the Boltzmann constant and \mathbf{p}_i is the probability associated with the i -th microstate. The positive real condition imposed on the nonextensivity parameter q ensures the stability of the Tsallis entropy [2]. The q -deformed logarithm made use of in (1.1) and its inverse the q -exponential are defined below

$$\ln_q x = \frac{x^{1-q} - 1}{1 - q}, \quad \exp_q(x) = [1 + (1 - q)x]_+^{\frac{1}{1-q}}, \quad (1.2)$$

where we have used the notation $[x]_+ = \max \{0, x\}$. In the $q \rightarrow 1$ limit, (1.1) reduces to the extensive Boltzmann-Gibbs entropy. A detailed account on the properties of the q -entropy and its applications may be found in [3].

To describe a system in thermodynamic equilibrium with its surroundings, we need three macroscopic variables corresponding to thermal, mechanical and chemical equilibrium. A system with fixed values of these parameters can exist in different microstates. A collection of systems existing in all the possible microstates corresponding to the same value of the macroscopic variables is called an ensemble. Each of these macroscopic parameters can be chosen between an extensive and an intensive variable. Thus we have eight different ways of choosing the three variables and consequently eight different ensembles. The eight ensembles can be divided into two different classes namely the isothermal class and the adiabatic class. In the isothermal class of ensembles, the thermal equilibrium variable is the temperature and the individual members of the ensemble are at the same temperature. The canonical, isothermal-isobaric [4-6], grandcanonical and the generalized ensemble [4,5] belong to the isothermal class. Each one of these isothermal ensembles is characterized by an heat function and a free energy. A general expression for the heat function and the generalized free energy are given below.

$$\mathfrak{H} = U + \sum_{\{\ell\}} x_\ell X_\ell \quad (1.3)$$

$$\mathcal{F} = U - TS + \sum_{\{\ell\}} x_\ell X_\ell \quad (1.4)$$

where X is an extensive thermodynamic quantity whose intensive conjugate is x . The index ℓ can take three different values of either 0, 1 or 2. In the $\ell = 0$ case the internal energy and the Helmholtz free energy are the heat function and the free energy respectively. The ensemble pertaining to this situation is the canonical ensemble (N, V, T) . Both the isothermal-isobaric (N, P, T) and the grandcanonical (μ, V, T) ensemble relate to the $\ell = 1$ case in (1.3) and (1.4). The enthalpy $H = U + PV$ and the Gibbs free energy $G = U - TS + PV$ are the heat function and the free energy corresponding

to the isothermal-isobaric ensemble. For the grandcanonical ensemble the Hill energy $L = U - \mu N$ and the $\Phi = U - TS - \mu N$ are the heat function and the free energy respectively. The $\ell = 2$ case describes the completely open system (μ, P, T) and the ensemble is usually referred to as the generalized ensemble. The R function $R = U + PV - \mu N$ and $\mathcal{E} = U + PV - TS - \mu N$ are the heat function and the free energy of the generalized ensemble. The adiabatic class of ensembles arise when the thermal equilibrium happens with respect to the heat function which is an extensive quantity. Based on the four different heat functions namely U, H, L and R we have four different ensembles. The well known microcanonical (N, V, U) ensemble. The isoenthalpic-isobaric (N, P, H) ensemble introduced in [7] and later extensively studied in references [8,9]. More recently the adiabatic ensemble with number fluctuations (μ, V, L) and the adiabatic ensemble with number and volume fluctuations (μ, P, R) were introduced through references [10] and [11] respectively. All the four adiabatic ensembles were treated in a unified way in [12]. Of the eight ensembles, the microcanonical, the canonical and the grandcanonical ensembles have been extensively studied and are well known in statistical mechanics. But the other five ensembles are also of fundamental importance in studying physical problems whose experimental conditions emulate the conditions of these ensembles. For example the isothermal-isobaric and the isoenthalpic-isobaric ensembles are used to study fluids which are confined at constant pressure. A molecular dynamic simulation for these ensembles was evolved in [13]. The generalized ensemble has been studied in [14]. Applications of the generalized ensemble include lattice gas models, and a system of polymer molecule of N monomers held together by weak forces such that the number N fluctuates [14].

An investigation on the ensemble formulation of nonextensive statistical mechanics based on q -entropy (1.1) was initiated in [1] through the study of two level system in the microcanonical and the canonical ensembles. A further detailed study of the canonical ensemble was carried out in references [15,16] wherein the second and the third constraint models were introduced. In the second constraint method [15] we use the unnormalized q -expectation value which, for a given observable O reads:

$$\langle O \rangle_q^{(2)} = \sum_j \left(\mathbf{p}_j^{(2)}(\beta) \right)^q O_j, \quad \langle 1 \rangle_q^{(2)} \equiv \mathbf{c}^{(2)}(\beta) = \sum_j \left(\mathbf{p}_j^{(2)}(\beta) \right)^q, \quad (1.5)$$

where $\mathbf{p}_j^{(2)}$ is the ensemble probability of the microstate j in the second constraint. Though the thermodynamic Legendre structure is preserved in the second constraint, the formalism suffered from certain disadvantages. The unit operator does not preserve its norm for an arbitrary value of q and, the form of the energy conservation principle in the macroscopic and microscopic limits varied. In order to overcome the disadvantages in the second constraint, an appropriately normalized form of the q -expectation value known as the third constraint method was introduced in [16]. The definition of the q -expectation in the third constraint formalism is

$$\langle O \rangle_q^{(3)} = \frac{\sum_j \left(\mathbf{p}_j^{(3)}(\beta) \right)^q O_j}{\mathbf{c}^{(3)}(\beta)}, \quad \mathbf{c}^{(3)}(\beta) = \sum_j \left(\mathbf{p}_j^{(3)}(\beta) \right)^q. \quad (1.6)$$

Though the third constraint method cleared all the problems previously encountered in the second constraint method, the probabilities became implicit quantities rendering

the calculations difficult. But fortunately, the second and the third constraint models can be interrelated via a temperature transformation relation which helps us to override the difficulties caused by the implicitness in the probabilities and the thermodynamic variables. The various applications of the canonical formulation may be found in [17,18]. A similar formulation of the grandcanonical ensemble was first done in the second constraint [19] and later in the third constraint [20]. A detailed investigation of the microcanonical ensemble based on the q -entropy (1.1) was carried out in [21] and the classical ideal gas was discussed as an application. Thus in the nonextensive statistical mechanics, based on q -entropy only three ensembles, the canonical [1,15,16] the microcanonical [1,21] and the grandcanonical [19,20] have been investigated so far.

In the current work we present two unified frameworks one for the isothermal class of ensembles and the other for the adiabatic class of ensembles. The unified framework pertaining to the isothermal class of ensembles has been presented for both the second and the third constraint formalisms though the latter is the currently accepted formulation. Adequate explanation for providing a unified formulation for the second constraint formalism is discussed at the relevant places in the article. A generalized formulation of the temperature transformation relation has been constructed to interrelate the second and the third constraint formulations. An exact solution of the specific heats at constant pressure and at constant volume corresponding to both the classical nonrelativistic ideal gas and the extreme relativistic ideal gas has been obtained in the isothermal isobaric ensemble. Contrarily obtaining an exact solution to these ideal gas models in the grandcanonical and the generalized ensemble appears to be difficult. We make use of the technique of disentangling of q -exponential into a series of ordinary exponentials [22] to construct a perturbative approach to the problem. Such an approach has already been used in the context of the canonical ensembles [18,23]. In the case of grandcanonical ensemble, the perturbative terms up to second order in the expansion parameter $(1 - q)$ has been retained. The perturbative terms have been displayed up to first order in the expansion parameter $(1 - q)$ in the case of the generalized ensemble. The limitations imposed on the order of $(1 - q)$ is only for the sake of simplicity and in practice the method could be extended to any arbitrary order in the perturbative parameter. A unified framework to describe all the four adiabatic ensembles in the nonextensive q -statistics has been put forward. A q -generalization of the equipartition theorem and the virial theorem have also been discussed. The specific heat at constant pressure and at constant volume corresponding to the nonrelativistic and extreme relativistic models of ideal gas have been exactly computed. Since a summation over the number of particles could not be evaluated in the (μ, V, L) and the (μ, P, R) adiabatic ensembles, the phase space volume and the equation of state are expressed as formal sums. Throughout the article we identify the temperature with the Lagrange multiplier corresponding to the constraint on the internal energy. This is because if we assume the notion of quasireversibility and simultaneously implement the first law of thermodynamics the Tsallis entropy becomes identical to the thermodynamic Clausius entropy [24] only when the Lagrange multiplier β is associated with the inverse temperature.

The plan of this article is as follows: The unified framework for the isothermal ensembles is presented in Section II, wherein the second and third constraint formulations are described as separate subsections. Using the classical nonrelativistic and extreme rela-

tivistic ideal gases the isothermal-isobaric ensemble, the grandcanonical ensemble and the generalized ensemble are illustrated in Sections III, IV and V. A generalized formulation of the adiabatic ensembles is given in Section VI. The ideal gas model in the isoenthalpic-isobaric ensemble have been worked out in Section VII. In Sections VIII and IX the (μ, V, L) and the (μ, P, R) ensembles are discussed. We present our concluding remarks in Section X.

II Isothermal ensemble

The isothermal class of ensembles is used to study systems in which the thermal equilibration is with respect to the temperature. A unified framework to study the isothermal class of ensembles is introduced in this section. This section is divided into two subsections. In the first subsection a unified formulation of the unnormalized q -expectation values or the second constraint formalism is presented. A similar unified method of the third constraint formalism is presented in the second subsection. Finally we demonstrate the interrelation between the two formalisms and derive a generalized expression for the temperature transformation relation.

A. Second constraint

The expectation values of energy, a general thermodynamic observable and the heat function based on the unnormalized q -expectation value (1.5) is

$$U_q^{(2)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta) = \sum_{i, X_{\{\ell\}}} \left(\mathbf{p}_{i: X_{\{\ell\}}}^{(2)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta) \right)^q \epsilon_i, \quad (2.1)$$

$$X_{\ell: q}^{(2)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta) = \sum_{i, X_{\{\ell\}}} \left(\mathbf{p}_{i: X_{\{\ell\}}}^{(2)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta) \right)^q X_\ell. \quad (2.2)$$

$$\mathfrak{H}_q^{(2)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta) = \sum_{i, X_{\{\ell\}}} \left(\mathbf{p}_{i: X_{\{\ell\}}}^{(2)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta) \right)^q \left(\epsilon_i + \sum_{\{\ell\}} x_\ell X_\ell \right) \quad (2.3)$$

where $\mathbf{p}_{i: X_{\{\ell\}}}^{(2)}$ is the probability of finding a particle in a particular microstate and X is an extensive thermodynamic quantity whose intensive counterpart is x . The chemical and the mechanical equilibrium variables are denoted by \mathfrak{x}_1 and \mathfrak{x}_2 . A brief introduction of the variable ℓ and the method to deduce the various ensembles corresponding to its different values is given in Section I.

Optimization of the entropy (1.1) using the normalization condition, the internal energy (2.1) and the other extensive thermodynamic variables (2.2) leads to the distribution given below

$$\mathbf{p}_{i: X_{\{\ell\}}}^{(2)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta) = \frac{1}{Z_q^{(2)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta)} \exp_q \left(-\beta \left(\epsilon_i + \sum_{\{\ell\}} x_\ell X_\ell \right) \right), \quad (2.4)$$

where $\mathcal{Z}_q^{(2)}$ the partition function in the second constraint is

$$\mathcal{Z}_q^{(2)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta) = \sum_{i, X_{\{\ell\}}} \exp_q \left(-\beta \left(\epsilon_i + \sum_{\{\ell\}} x_\ell X_\ell \right) \right). \quad (2.5)$$

As previously stated in section I, we associate the temperature with the Lagrange multiplier corresponding to the internal energy i.e., $\beta = 1/kT$.

The second constraint heat function of a given ensemble $(\mathfrak{X}_1, \mathfrak{X}_2, \beta)$ can be computed from the partition function using

$$\mathfrak{H}_q^{(2)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta) = -\frac{\partial}{\partial \beta} \ln_q \mathcal{Z}_q^{(2)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta). \quad (2.6)$$

In terms of the partition function the extensive variable in the second constraint is

$$X_{\ell;q}^{(2)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta) = -\frac{1}{\beta} \frac{\partial}{\partial x_\ell} \ln_q \mathcal{Z}_q^{(2)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta). \quad (2.7)$$

The knowledge of the heat function and the extensive thermodynamic variables of a given ensemble enables us to find the internal energy using Legendre transformation.

The thermodynamic potential corresponding to an ensemble in the second constraint formulation is the generalized free energy

$$\mathcal{F}_q^{(2)} = -kT \ln_q \mathcal{Z}_q^{(2)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta), \quad (2.8)$$

from which the entropy and the other extensive variables are computed as follows:

$$S_q = -\frac{\partial \mathcal{F}_q^{(2)}}{\partial T} \Big|_P, \quad X_{\ell;q}^{(2)} = \frac{\partial \mathcal{F}_q^{(2)}}{\partial x_\ell} \Big|_T. \quad (2.9)$$

The thermodynamic expression for the specific heats corresponding to the different conditions is

$$C_q^{(2)}|_V = \frac{\partial U_q^{(2)}}{\partial T} \Big|_V, \quad C_q^{(2)}|_{x_{\{\ell\}}} = -T \frac{\partial^2 \mathcal{F}_q^{(2)}}{\partial T^2} \Big|_{x_{\{\ell\}}} = T \frac{\partial S_q}{\partial T}. \quad (2.10)$$

B. Third constraint formalism

To overcome the failures of the second constraint we use the normalized q -expectation values in the third constraint formalism. The definition of the internal energy, an arbitrary extensive variable and the heat function in this formalism are

$$U_q^{(3)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta) = \frac{1}{\mathfrak{c}^{(3)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta)} \sum_{i, X_{\{\ell\}}} \left(\mathfrak{p}_{i:X_{\{\ell\}}}^{(3)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta) \right)^q \epsilon_i, \quad (2.11)$$

$$X_{\ell;q}^{(3)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta) = \frac{1}{\mathfrak{c}^{(3)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta)} \sum_{i, X_{\{\ell\}}} \left(\mathfrak{p}_{i:X_{\{\ell\}}}^{(3)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta) \right)^q X_\ell, \quad (2.12)$$

$$\mathfrak{H}_q^{(3)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta) = \frac{1}{\mathfrak{c}^{(3)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta)} \sum_{i, X_{\{\ell\}}} \left(\mathfrak{p}_{i:X_{\{\ell\}}}^{(3)}(\mathfrak{X}_1, \mathfrak{X}_2, \beta) \right)^q \left(\epsilon_i + \sum_{\{\ell\}} x_\ell X_\ell \right), \quad (2.13)$$

where $\mathbf{p}_{i:X_{\{\ell\}}}^{(3)}$ is the probability of finding the particle in a particle microstate. The factor $\mathbf{c}^{(3)}$ is the sum of q -weights in the third constraint and is defined as

$$\mathbf{c}^{(3)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta,) = \sum_{i, X_{\{\ell\}}} \left(\mathbf{p}_{i:X_{\{\ell\}}}^{(3)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta) \right)^q. \quad (2.14)$$

Along with the normalization condition, the definitions corresponding to the internal energy (2.11) and the arbitrary extensive variable (2.12) are used in the optimization of the entropy (1.1). The probability distribution obtained through this procedure is

$$\mathbf{p}_{i:X_{\{\ell\}}}^{(3)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta) = \frac{1}{\bar{\mathcal{Z}}_q^{(3)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta)} \exp_q \left(- \frac{\beta}{\mathbf{c}^{(3)}(\mathfrak{x}_1, \mathfrak{x}_2, \beta)} \left(\epsilon_i + \sum_{\{\ell\}} x_\ell X_\ell - \mathfrak{H}_q^{(3)} \right) \right), \quad (2.15)$$

where $\mathfrak{H}_q^{(3)}$ is the heat function in the third constraint and $\beta = 1/kT$. The generalized partition function $\bar{\mathcal{Z}}_q^{(3)}$ in (2.15) is as defined below:

$$\bar{\mathcal{Z}}_q^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2) = \sum_{i, X_{\{\ell\}}} \exp_q \left(- \frac{\beta}{\mathbf{c}^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2)} \left(\epsilon_i + \sum_{\{\ell\}} x_\ell X_\ell - \mathfrak{H}_q^{(3)} \right) \right). \quad (2.16)$$

The generalized partition function and the sum of the q -weights are related via the expression

$$(\bar{\mathcal{Z}}_q^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2))^{1-q} = \mathbf{c}^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2), \quad (2.17)$$

which holds for all the isothermal ensembles and plays a crucial role in solving the implicit equations in the third constraint.

The heat function in the third constraint satisfies the differential equation

$$\beta \frac{\partial}{\partial \beta} \mathfrak{H}_q^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2) = \frac{\partial}{\partial \beta} \ln_q \bar{\mathcal{Z}}_q^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2). \quad (2.18)$$

From the knowledge of the heat function $\mathfrak{H}_q^{(3)}$, and the generalized partition function $\bar{\mathcal{Z}}_q^{(3)}$ the expectation value of the extensive thermodynamic variable is found using

$$X_{\ell;q}^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2) = \frac{\partial}{\partial x_\ell} \left(\mathfrak{H}_q^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2) - \frac{1}{\beta} \ln_q \bar{\mathcal{Z}}_q^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2) \right). \quad (2.19)$$

The internal energy can be obtained from the heat function and the extensive thermodynamic quantities using Legendre transformation. Making use of the property (2.17), the nonextensive entropy (1.1) expressed in terms of the generalized partition function (2.16) is

$$S_q = k \ln_q \bar{\mathcal{Z}}_q^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2). \quad (2.20)$$

Substituting the entropy (2.20) in (1.4) we arrive at the free energy in the third constraint as

$$\mathcal{F}_q^{(3)} = U_q^{(3)} - \frac{1}{\beta} \ln_q \bar{\mathcal{Z}}_q^{(3)}(\beta, \mathfrak{x}_1, \mathfrak{x}_2) + \sum_{\{\ell\}} x_\ell X_{\ell;q}^{(3)}. \quad (2.21)$$

In terms of the generalized free energy defined in (2.21) the heat function and the q -expectation value of the extensive thermodynamic variable reads:

$$\mathfrak{H}_q^{(3)} = \frac{\partial}{\partial \beta}(\beta \mathcal{F}_q^{(3)}), \quad X_{\ell;q}^{(3)} = \frac{\partial \mathcal{F}_q^{(3)}}{\partial x_\ell}. \quad (2.22)$$

The heat capacities at constant pressure and at constant volume in the third constraint are

$$C_q^{(3)} \Big|_V = \frac{\partial U_q^{(3)}}{\partial T}, \quad (2.23)$$

$$C_q^{(3)} \Big|_{x_{\{\ell\}}} = \frac{\partial \mathfrak{H}_q^{(3)}}{\partial T} = T \frac{\partial S_q}{\partial T} = -T \frac{\partial^2 \mathcal{F}_q^{(3)}}{\partial T^2}. \quad (2.24)$$

The third constraint approach is the currently accepted formulation of nonextensive statistical mechanics and problems which do not involve simulations can be solved directly in this approach. In the case of Montecarlo and molecular dynamics simulations direct use of the third constraint is difficult. To overcome this, the calculations are initially performed in the second constraint and the results are then transferred to the corresponding quantities in the third constraint. The transformation relation for the canonical ensemble was introduced in [16]. Adopting a similar procedure for the unified framework of isothermal ensembles, the probabilities in the second and the third constraint formalisms (2.4, 2.15) are related as follows

$$\mathbf{p}_{i:X_{\{\ell\}}}^{(3)}(\beta, \mathfrak{X}_1, \mathfrak{X}_2) = \mathbf{p}_{i:X_{\{\ell\}}}^{(2)}(\beta', \mathfrak{X}_1, \mathfrak{X}_2) = \exp_q \left(-\beta' \left(\epsilon_i + \sum_{\{\ell\}} x_\ell X_\ell \right) \right) (\mathcal{Z}_q^{(2)}(\beta', \mathfrak{X}_1, \mathfrak{X}_2))^{-1}, \quad (2.25)$$

where, the pseudoinverse temperature β' is related to β as

$$\beta' = \frac{\beta}{\mathbf{c}^{(3)}(\beta, \mathfrak{X}_1, \mathfrak{X}_2) + (1-q) \beta \mathfrak{H}_q^{(3)}(\beta, \mathfrak{X}_1, \mathfrak{X}_2)}. \quad (2.26)$$

The relation in (2.26) is inverted to obtain β' in terms of β

$$\beta = \beta' \frac{\mathbf{c}^{(2)}(\beta', \mathfrak{X}_1, \mathfrak{X}_2)}{1 - (1-q) \beta' \frac{\mathfrak{H}_q^{(2)}(\beta', \mathfrak{X}_1, \mathfrak{X}_2)}{\mathbf{c}^{(2)}(\beta', \mathfrak{X}_1, \mathfrak{X}_2)}}. \quad (2.27)$$

After obtaining the transformation pertinent to a given system, there are two independent methods through which we can get the other thermodynamic variables.

(i) Probability transformation technique: In this method, introduced in Ref. [16], the sum of q -weights is transformed from the second constraint to the third constraint using the temperature transformation relation (2.27). Using (2.17) the generalized partition function is obtained from the sum of q -weights from which we can calculate the specific heat directly.

(ii) Observable transformation technique: Any dynamical observable in the second constraint can be transformed to the corresponding one in the third constraint [23] through the relation given below

$$O_q^{(3)}(\beta, \mathfrak{X}_1, \mathfrak{X}_2) = \frac{O_q^{(2)}(\beta', \mathfrak{X}_1, \mathfrak{X}_2)}{\mathbf{c}^{(2)}(\beta', \mathfrak{X}_1, \mathfrak{X}_2)}. \quad (2.28)$$

All the relevant thermodynamic quantities of a given ensemble in the third constraint can be computed from the second constraint using the two methods described above.

The thermodynamic relations for the canonical ensemble can be obtained from the unified framework by observing that the internal energy and the Helmholtz free energy are the heat function and the free energy respectively. An elaborate exposition on the canonical ensemble may be found in [15,16] and since this ensemble has been investigated in detail we do not intend to discuss it anymore.

III Isothermal-Isobaric ensemble

The isothermal-isobaric ensemble is used to study systems which attain equilibrium by exchanging both internal energy and volume with the heat bath. The enthalpy and the Gibbs free energy plays the role of heat function and free energy respectively. Using the unified framework described in Section II the nonrelativistic and the extreme relativistic ideal gases are investigated.

A. Nonrelativistic Ideal gas

The Hamiltonian of a classical ideal gas in the non-relativistic regime with particles possessing momenta \mathbf{p}_i ($i = 1, \dots, N$) in D dimensions is

$$\mathcal{H}_{nr}(p) = \sum_i \frac{p_i^2}{2m}, \quad p_i = |\mathbf{p}_i|. \quad (3.1)$$

The generalized partition function corresponding to the third constraint in the (N, P, T) ensemble is

$$\begin{aligned} \bar{Y}_q^{(3)}(\beta, P) &= \frac{1}{N! h^{DN}} \int_V dV \int_{r_i} \int_{p_i} \prod_{i=1}^N d^D r_i d^D p_i \times \\ &\times \exp_q \left(-\frac{\beta}{c^{(3)}} \left(\sum_i \frac{p_i^2}{2m} - U_q^{(3)} + PV - PV_q^{(3)} \right) \right). \end{aligned} \quad (3.2)$$

Carrying out the phase space integration in (3.2), we arrive at

$$\bar{Y}_q^{(3)}(\beta, P) = \frac{\mathcal{M}^N}{N!} \frac{\Gamma\left(\frac{2-q}{1-q}\right)}{\Gamma\left(\frac{2-q}{1-q} + \frac{DN}{2}\right)} \int_V V^N \left(\exp_q \left(\frac{\beta}{c^{(3)}} (U_q^{(3)} - PV + PV_q^{(3)}) \right) \right)^\Lambda dV, \quad (3.3)$$

where $\mathcal{M} = \left(\frac{2\pi m}{h^2}\right)^{D/2}$ and $\Lambda = 1 + (1-q)DN/2$. In order to express the thermodynamic variables in a simplified manner, we define the following quantities

$$\Lambda_\kappa = 1 + (1-q)\mathfrak{D}_\kappa, \quad \mathfrak{L}_\kappa = (1 - (1-q)\mathfrak{D}_\kappa)^{-1}, \quad \mu_\kappa = \Lambda_\kappa \mathfrak{L}_\kappa, \quad (3.4)$$

where $\kappa = 1(2)$ for a non-relativistic (extreme relativistic) case and $\mathfrak{D}_1 = \frac{DN}{2} + N$ ($\mathfrak{D}_2 = DN + N$). Integrating over volume in (3.3) we arrive at the generalized partition

function

$$\bar{Y}_q^{(3)}(\beta, P) = \frac{\mathcal{M}^N \Gamma\left(\frac{2-q}{1-q}\right)}{\Gamma\left(\frac{2-q}{1-q} + \mathfrak{D}_1 + 1\right)} \left(\frac{1}{1-q}\right)^{\mathfrak{D}_1+1} \left(\exp_q\left(\frac{\beta}{\mathfrak{c}^{(3)}}(U_q^{(3)} + PV_q^{(3)})\right)\right)^{\Lambda_1-(1-q)} \left(\frac{\mathfrak{c}^{(3)}}{\beta}\right)^{\mathfrak{D}_1+1} \left(\frac{1}{P}\right)^{N+1}. \quad (3.5)$$

It is interesting to note that (3.5) has the dimensions of volume. This is due to the overcounting of volume eigenstates in systems in which the volume is a continuous variable. To overcome this we use the shell particle method of counting of volume states [25,26]. In the shell particle method of counting we take into account only the minimum volume needed to confine a particular configuration. When there are many equivalent ways of choosing a minimum volume we treat all of them as the same volume eigenstate. The minimum volume is fixed by enforcing a condition where we require that at least one particle lies on the boundary of the system. Carrying out the volume integral of the generalized partition function using the shell particle counting technique to reject the redundant volume states we arrive at

$$\bar{Y}_q^{(3)}(\beta, P) = \mathcal{M}^N \mathcal{G}_1 \left(\exp_q\left(\frac{\beta}{\mathfrak{c}^{(3)}}(U_q^{(3)} + PV_q^{(3)})\right)\right)^{\Lambda_1} \left(\frac{\mathfrak{c}^{(3)}}{\beta}\right)^{\mathfrak{D}_1} \left(\frac{1}{P}\right)^N. \quad (3.6)$$

The above expression of the generalized partition function (3.6) in contrast to (3.5), is dimensionless making it consistent with the basic principles of statistical mechanics. The ratio of gamma functions \mathcal{G}_1 made use of in (3.6) is

$$\mathcal{G}_1 = \frac{\Gamma\left(\frac{2-q}{1-q}\right)}{(1-q)^{\mathfrak{D}_1} \Gamma\left(\frac{2-q}{1-q} + \mathfrak{D}_1\right)}. \quad (3.7)$$

The heat function of the isothermal-isobaric ensemble given by the basic relation (2.13) is computed and the result is

$$H_q^{(3)} = \mathfrak{D}_1 \frac{\mathcal{M}^N}{\bar{Y}_q^{(3)}} \mathcal{G}_1 \left(\exp_q\left(\frac{\beta}{\mathfrak{c}^{(3)}}H_q^{(3)}\right)\right)^{\Lambda_1} \left(\frac{1}{P}\right)^N \left(\frac{\mathfrak{c}^{(3)}}{\beta}\right)^{\mathfrak{D}_1+1}. \quad (3.8)$$

The ratio between the (3.6) and (3.8) is computed

$$H_q^{(3)} = \mathfrak{D}_1 \frac{\mathfrak{c}^{(3)}}{\beta}. \quad (3.9)$$

Using (3.9) in conjunction with (2.17), in (3.6) the explicit form of the generalized partition function is

$$\bar{Y}_q^{(3)} = (\mathcal{M}^N \mathcal{G}_1)^{\mathfrak{L}_1} (\exp_q(\mathfrak{D}_1))^{\mu_1} \left(\frac{1}{\beta}\right)^{\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P}\right)^{N \mathfrak{L}_1}. \quad (3.10)$$

Similarly the explicit expression of the enthalpy computed through the use of (3.8), (3.10) and (2.17) is

$$H_q^{(3)} = \frac{\mathfrak{D}_1}{\beta} \Xi_{nr} \left(\frac{1}{\beta}\right)^{(1-q)\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P}\right)^{(1-q)N \mathfrak{L}_1}, \quad (3.11)$$

where the constant factor Ξ_{nr} used in (3.11) is

$$\Xi_{nr} = (\mathcal{M}^N \mathcal{G}_1)^{(1-q)\mathfrak{L}_1} \Lambda_1^{\mu_1}. \quad (3.12)$$

The entropy of the system in the third constraint written down from the generalized partition function using the relation (2.20) is

$$S_q = \frac{k}{1-q} \left[\Xi_{nr} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_1} - 1 \right]. \quad (3.13)$$

Making use of the thermodynamic Legendre structure (2.21) the Gibbs free energy of the classical ideal gas is obtained:

$$G_q^{(3)} = \frac{1}{(1-q)\beta} \left[((1-q)\mathfrak{D}_1 - 1) \Xi_{nr} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_1} - 1 \right]. \quad (3.14)$$

The average volume of the classical nonrelativistic ideal gas in the third constraint can be found via the expression (2.19) using the explicit expression of the generalized partition function (3.10) and the enthalpy (3.11). The calculated expression of the average volume reads:

$$V_q^{(3)} = \frac{N}{\beta P} \Xi_{nr} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_1}. \quad (3.15)$$

The average volume which was computed using enthalpy can also be calculated through two other different methods. The first method is based on a specific form of (2.22) applicable to the isothermal-isobaric ensemble in which the average volume is related to the Gibbs free energy. The second method makes use of the defining relation of the average volume (2.12) to obtain an implicit expression. Using the implicit expression in conjunction with (3.11), (3.10) and (2.17) we can obtain the final explicit form. The results obtained through both these methods are in agreement with that obtained in (3.15). Rewriting the expression for the average volume (3.15) we arrive at the nonextensive form of the equation of state corresponding to the isothermal-isobaric ensemble

$$PV_q^{(3)} = \frac{N}{\beta} \Xi_{nr} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_1}. \quad (3.16)$$

From the knowledge of the enthalpy and the average volume, the internal energy evaluated using the Legendre structure is

$$U_q^{(3)} = \frac{DN}{2\beta} \Xi_{nr} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_1}. \quad (3.17)$$

The defining relation of the internal energy (2.11) has been used to verify (3.17) in a manner analogous to the calculation of the average volume.

The specific heat at constant pressure can be found from either the enthalpy (3.11) or entropy (3.13) or the Gibbs free energy (3.14) using (2.24)

$$C_q^{(3)}|_P = \left(\frac{DN}{2} + N \right) k \mathfrak{L}_1 \Xi_{nr} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_1}. \quad (3.18)$$

From the internal energy (3.17) the specific heat at constant volume is evaluated through the use of (2.23)

$$C_q^{(3)}|_V = \frac{DN}{2} k \Xi_{nr} \mathfrak{L}_1 \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_1}. \quad (3.19)$$

The difference between the specific heat at constant pressure (3.18) and the specific heat at constant volume (3.19) is

$$C_q^{(3)}|_P - C_q^{(3)}|_V = Nk \mathfrak{L}_1 \Xi_{nr} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_1 \mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_1}, \quad (3.20)$$

which is the generalized form of Meyer's relation and in the extensive limit the lhs goes as Nk . It is interesting to note that the factor γ expressing the ratio between the two specific heats

$$\gamma = \frac{C_q^{(3)}|_P}{C_q^{(3)}|_V} = 1 + \frac{2}{D}, \quad (3.21)$$

is independent of the nonextensive parameter q and the number of particles N , though the specific heats (3.18) and (3.19) depend on these parameters explicitly.

The thermodynamic quantities calculated in this section can also be evaluated in a different method where we compute the thermodynamic quantities in the second constraint framework. The ensemble probabilities in the second and the third constraints are related through a fictitious temperature β' as given in equation (2.25). This fictitious temperature β' in the second constraint is related to the original temperature β in the third constraint through a transformation. The temperature transformation relation corresponding to the classical ideal gas in the isothermal-isobaric ensemble is

$$\frac{1}{\beta'} = (\mathcal{M}^N \mathcal{G}_1)^{(1-q)\mathfrak{L}_1} \Lambda_1^{2\mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_1} \left(\frac{1}{\beta} \right)^{\mathfrak{L}_1}. \quad (3.22)$$

Using the above transformation the third constraint thermodynamic quantities can be computed using the probability transformation technique or the observable transformation technique. The thermodynamic quantities and the equation of state obtained through this transformation method are identical to the corresponding quantities computed directly in the third constraint.

B. Extreme relativistic ideal gas

The Hamiltonian of the extreme relativistic classical ideal gas in D dimensions is

$$\mathcal{H}_{er}(p) = c \sum_i p_i, \quad p_i = |\mathbf{p}_i|, \quad (3.23)$$

where the factor c is the velocity of light. The nonextensive study of the Hamiltonian (3.23) is carried out in the isothermal-isobaric ensemble. Since the calculational procedure is identical to the nonrelativistic case we present only the core steps leading to the

calculation of the specific heats. The generalized partition function calculated using the basic definition is

$$\bar{Y}_q^{(3)} = \Delta^N \mathcal{G}_2 \left(\frac{1}{P} \right)^N \left(\frac{\mathfrak{c}^{(3)}}{\beta} \right)^{DN+N}. \quad (3.24)$$

The notations made use of in (3.24) are

$$\Delta = \frac{2\pi^{D/2}\Gamma(D)}{(ch)^D\Gamma(D/2)}, \quad \mathcal{G}_2 = \frac{\Gamma\left(\frac{2-q}{1-q}\right)}{(1-q)^{\mathfrak{D}_2} \Gamma\left(\frac{2-q}{1-q} + \mathfrak{D}_2\right)} \quad (3.25)$$

Equation (3.24) is an implicit equation since it is a function of the sum of q -weights which is related to the generalized partition function through the relation (2.17). The nonextensive enthalpy of the extreme relativistic ideal gas is

$$H_q^{(3)} = \mathfrak{D}_2 \frac{\Delta^N}{\bar{Y}_q^{(3)}} \mathcal{G}_2 \left(\exp_q \left(\frac{\beta}{\mathfrak{c}^{(3)}} H_q^{(3)} \right) \right)^{\Lambda_2} \left(\frac{1}{P} \right)^N \left(\frac{\mathfrak{c}^{(3)}}{\beta} \right)^{\mathfrak{D}_2+1} \quad (3.26)$$

where the factors Λ_2 , \mathfrak{L}_2 and μ_2 used in this section are described in (3.4) and the discussions following it. The ratio between (3.24) and (3.26) is

$$H_q^{(3)} = \mathfrak{D}_2 \frac{\mathfrak{c}^{(3)}}{\beta}. \quad (3.27)$$

Using (3.27) in (3.24) we obtain the explicit expression corresponding to the generalized partition function

$$\bar{Y}_q^{(3)} = (\Delta^N \mathcal{G}_2)^{\mathfrak{L}_2} (\exp_q(\mathfrak{D}_2))^{\mu_2} \left(\frac{1}{P} \right)^{N\mathfrak{L}_2} \left(\frac{1}{\beta} \right)^{\mathfrak{D}_2\mathfrak{L}_2}. \quad (3.28)$$

Similarly the calculated value of the explicit form of the enthalpy is

$$H_q^{(3)} = \frac{\mathfrak{D}_2}{\beta} \Xi_{er} \left(\frac{1}{P} \right)^{(1-q)N\mathfrak{L}_2} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_2\mathfrak{L}_2}, \quad (3.29)$$

where the factor Ξ_{er} is defined as

$$\Xi_{er} = (\Delta^N \mathcal{G}_2)^{(1-q)\mathfrak{L}_2} \Lambda_2^{\mu_2}. \quad (3.30)$$

The average volume of the extreme relativistic ideal gas is evaluated through the use of (6.7). The equation of state obtained by rewriting the expression for the average volume is

$$PV_q^{(3)} = \frac{N}{\beta} \Xi_{er} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_2\mathfrak{L}_2} \left(\frac{1}{P} \right)^{(1-q)N\mathfrak{L}_2}. \quad (3.31)$$

To find the internal energy we use the Legendre transform (1.3) and the expressions for the enthalpy and the average volume. The computed expression of the internal energy reads:

$$U_q^{(3)} = \frac{DN}{\beta} \Xi_{er} \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_2\mathfrak{L}_2} \left(\frac{1}{P} \right)^{(1-q)N\mathfrak{L}_2}. \quad (3.32)$$

The specific heat capacity of the extreme relativistic ideal gas at constant volume and at constant pressure can be established from the final explicit expressions of the internal energy and the enthalpy respectively. We exhibit the results below

$$C_q^{(3)}|_V = DN k \Xi_{er} \mathfrak{L}_2 \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_2 \mathfrak{L}_2} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_2}, \quad (3.33)$$

$$C_q^{(3)}|_P = (DN + N) k \Xi_{er} \mathfrak{L}_2 \left(\frac{1}{\beta} \right)^{(1-q)\mathfrak{D}_2 \mathfrak{L}_2} \left(\frac{1}{P} \right)^{(1-q)N \mathfrak{L}_2}. \quad (3.34)$$

The ratio between the heat capacity at constant pressure and at constant volume

$$\frac{C_q^{(3)}|_P}{C_q^{(3)}|_V} = 1 + \frac{1}{D}, \quad (3.35)$$

is found to be independent of both the nonextensive parameter q and the number of particles N . All the results in this section have been calculated through two methods. In the first method, the third constraint generalized partition function, sum of q -weights and the enthalpy are computed. Since these quantities are implicit in nature, they are systematically solved to obtain the explicit forms. The second method is based on the interrelation between the second and the third constraint formalisms. The thermodynamic quantities are first obtained in the second constraint formalism and they are later transformed to the corresponding quantities in the third constraint through the use of the temperature transformation relation. Both the probability transformation and the observable transformation techniques are used in this objective. The results obtained through these methods are in precise agreement with each other. The proper counting of volume states advocated in references [25,26] has been used in both the methods. In the extensive $q \rightarrow 1$ limit, the standard physical quantities corresponding to the classical Boltzmann-Gibbs statistics are recovered.

Another interesting model is the Tonks gas [27] which is a one dimensional model of hard rod gas. The Hamiltonian describing the dynamics of a Tonks gas is

$$\mathcal{H}_{tg}(p) = \sum_i \frac{p_i^2}{2m} + V(r), \quad p_i = |\mathbf{p}_i|, \quad (3.36)$$

where the potential $V(r)$ is

$$\begin{aligned} V(r) &= 0 & x &\geq \sigma \\ &= \infty & x &< \sigma. \end{aligned} \quad (3.37)$$

An exact solution of the Tonks gas in the free length ensemble can be read from the results of the nonrelativistic ideal gas. In this discussion the term free length refers to the actual volume available for a particle $L_{f,q} = L - (N - 1)\sigma$. The equation of state of the Tonks gas in the free length ensemble can be read from the expression corresponding to the classical nonrelativistic ideal gas by observing that the number of dimensions is 1

and replacing the volume by the free length. The equation of state of the Tonks gas in the free length ensemble is

$$PL_{f;q}^{(3)} = \frac{N}{\beta} (\mathcal{M}_1^N \mathcal{G}_{1:1})^{(1-q)\mathfrak{L}_{1:1}} (\Lambda_{1:1})^{\mu_{1:1}} \left(\frac{1}{\beta}\right)^{\frac{3N}{2}\mathfrak{L}_{1:1}} \left(\frac{1}{P}\right)^{N\mathfrak{L}_{1:1}}, \quad (3.38)$$

where the functions $\mathcal{G}_{1:1}$ and $\Lambda_{1:1}$ are special cases of (3.7), obtained by substituting $D = 1$ and \mathcal{M}_1 is the 1 dimensional analog of \mathcal{M} . A direct computation of the Tonks gas is used to verify the expression for equation of state. The correct counting of volume states has been applied and the Boltzmann-Gibbs results are recovered in the $q \rightarrow 1$ limit.

IV Grand Canonical ensemble

A system which exchanges both the internal energy and the number of particles with its surroundings is described using grand canonical ensemble. The Hill energy $\mathbf{L} = U - \mu N$ is the heat function and the free energy is $\Phi = U - TS - \mu N$. In this section we extend the perturbative formulation developed in [18] and [23] to study the nonrelativistic and extreme relativistic ideal gas in grandcanonical ensemble.

A. Nonrelativistic classical ideal gas

A perturbative study of the nonrelativistic classical ideal gas described by the Hamiltonian (3.1) is carried out in the grand canonical ensemble. The generalized partition function in the third constraint is

$$\bar{Z}_q^{(3)}(\mu, V, \beta) = \sum_{N=0}^{\infty} \frac{1}{N! h^{DN}} \int d^{DN} r \, d^{DN} p \, \exp_q \left(-\tilde{\beta} \left(\sum_i \frac{p_i^2}{2m} - \mu N - \mathbf{L}_q^{(3)} \right) \right), \quad (4.1)$$

where $\tilde{\beta} = \frac{\beta}{\mathfrak{c}^{(3)}}$ and $\mathfrak{c}^{(3)}$ is the sum of q weights corresponding to the grand canonical ensemble in the third constraint. The Hill function $\mathbf{L}_q^{(3)} = U_q^{(3)} - \mu N_q^{(3)}$ is the heat function corresponding to the grand canonical ensemble where, $U_q^{(3)}$ and $N_q^{(3)}$ are the internal energy and the average number of particles respectively in the third constraint and μ is the chemical potential of the system.

The observation in [22], that the q exponential can be written as an infinite multiplicative series of ordinary exponential

$$\exp_q(x) = \prod_{k=1}^{\infty} \exp \left((-1)^{k-1} \frac{(1-q)^{k-1} x^k}{k} \right), \quad (4.2)$$

which in turn can be expanded up to any order in $(1-q)$, is used to construct a perturbative procedure for the generalized partition function. Assuming the generalized partition function (4.1) to be well defined in the region $q = 1$, we replace the q -exponential by the ordinary exponential. The resultant expression for the generalized partition function is:

$$\bar{Z}_q^{(3)}(\mu, V, \beta) = \hat{\mathcal{D}}_1(d_\beta) \exp(\mathcal{L}) \sum_{N=0}^{\infty} \frac{1}{N! h^{DN}} \int d^{DN} r \, d^{DN} p \, \exp \left(-\tilde{\beta} \left(\sum_i \frac{p_i^2}{2m} - \mu N \right) \right). \quad (4.3)$$

where $\mathcal{L} = \tilde{\beta} \mathcal{L}_q^{(3)}$ and the operator valued series $\widehat{\mathcal{D}}_1(d_\beta)$ in (4.3) is

$$\widehat{\mathcal{D}}_1(d_\beta) = 1 - \frac{(1-q)}{2} d_\beta^{(2)} + \frac{(1-q)^2}{3} \left(d_\beta^{(3)} + \frac{3}{8} d_\beta^{(4)} \right) + \dots, \quad d_\beta^{(n)} = \beta^n \frac{\partial^n}{\partial \beta^n}. \quad (4.4)$$

In the expression (4.3), we assume that the summation over the number of particles is a convergent, atleast in the region where the nonextensive parameter is close to 1. Carrying out the phase space integration and the summation over the number of particles in (4.3), the generalized partition function in the third constraint can be expressed as

$$\bar{Z}_q^{(3)}(\mu, V, \beta) = \widehat{\mathcal{D}}_1(d_\beta) \exp(\mathcal{L}) Z_{BG}(\tilde{\beta}), \quad (4.5)$$

where $Z_{BG}(\beta) = \exp(\exp(\beta\mu) V \mathcal{M} \beta^{-D/2})$ is the Boltzmann-Gibbs partition function. The perturbative series of the generalized partition function (4.5) calculated upto second order in the expansion parameter $(1-q)$ is

$$\bar{Z}_q^{(3)} = \exp(\mathcal{L}) Z_{BG}(\tilde{\beta}) (1 + (1-q) Z_1 + (1-q)^2 Z_2 + \dots), \quad (4.6)$$

where the coefficients of the perturbative series (4.6) are listed below

$$\begin{aligned} Z_1 &= \frac{1}{4} \left(2 \mathcal{L}^2 + 2 N_{BG}(\tilde{\beta}) (\alpha(\tilde{\beta}))^2 + (N_{BG}(\tilde{\beta}))^2 (2 (\alpha(\tilde{\beta}))^2 + 4 \alpha(\tilde{\beta}) \mathcal{L} + D) \right), \\ Z_2 &= \frac{1}{8} \mathcal{L}^4 + \frac{1}{3} \mathcal{L}^3 + \frac{1}{8} (N_{BG}(\tilde{\beta}))^4 (\alpha(\tilde{\beta}))^4 + \frac{1}{96} (N_{BG}(\tilde{\beta}))^3 (72 (\alpha(\tilde{\beta}))^4 + 12 \mathcal{L} (\alpha(\tilde{\beta}))^3 \\ &\quad + 4(8 (\tilde{\beta}\mu)^3 - 3D^2) \alpha(\tilde{\beta}) + D(4 (\tilde{\beta}\mu)^3 - D^2)) + \frac{1}{32} (N_{BG}(\tilde{\beta}))^2 (48 \mathcal{L} (\alpha(\tilde{\beta}))^2 \\ &\quad + 8 \mathcal{L} (3 \mathcal{L} + 2) (\alpha(\tilde{\beta}))^2 - 12 D \tilde{\beta}\mu \alpha(\tilde{\beta}) + 8(4 - 7D) (\tilde{\beta}\mu)^3 + 42 D^2 (\tilde{\beta}\mu)^2 \\ &\quad - 2D^2 (9 + 7D) \tilde{\beta} + D^2 (3 + 5D + 7D^2)) + \frac{1}{96} N_{BG}(\tilde{\beta}) \left(12 (\alpha(\tilde{\beta}))^4 \right. \\ &\quad \left. + 48 \mathcal{L} (\alpha(\tilde{\beta}))^3 + (72 \mathcal{L} - 48) \mathcal{L} (\alpha(\tilde{\beta}))^2 + (48 \mathcal{L}^3 + 72 \mathcal{L}^2 - 12 D^2) \alpha(\tilde{\beta}) \right. \\ &\quad \left. + 64 (\tilde{\beta}\mu)^3 - 12 D (\tilde{\beta}\mu)^2 + 24 D \tilde{\beta}\mu \mathcal{L} - D(4 + 9D - D^2) \right), \end{aligned} \quad (4.7)$$

The factor $\alpha(\tilde{\beta}) = \tilde{\beta} - \frac{D}{2}$ and the average number in the standard Boltzmann-Gibbs statistics is $N_{BG}(\beta) = \exp(\beta\mu) V \mathcal{M} \beta^{-D/2}$ are used in (4.7). We notice that the generalized partition function described above is an implicit quantity and depends on the heat function $\mathcal{L}_q^{(3)}$ and the sum of q -weights $\mathfrak{c}^{(3)}$ which is in turn related to the generalized partition function via the relation (2.17).

The integral form of the sum of q -weights written down from the defining relation (2.14) is

$$\begin{aligned} \mathfrak{c}^{(3)}(\mu, V, \beta) &= \frac{1}{\left(\bar{Z}_q^{(3)}(\mu, V, \beta) \right)^q} \times \\ &\times \sum_{N=0}^{\infty} \frac{1}{N! h^{DN}} \int d^{DN} r d^{DN} p \left(\exp_q \left(-\tilde{\beta} \left(\sum_i \frac{p_i^2}{2m} - \mu N - \mathcal{L}_q^{(3)} \right) \right) \right)^q. \end{aligned} \quad (4.8)$$

A perturbative computation of the sum of q -weights is evolved in the following manner, first the q -exponential is expressed in terms of the ordinary exponential

$$\begin{aligned} \mathfrak{c}^{(3)}(\mu, V, \beta) &= \frac{1}{\left(\bar{Z}_q^{(3)}(\mu, V, \beta)\right)^q} \widehat{\mathcal{D}}_2(d_\beta) \exp(\mathcal{L}) \times \\ &\times \sum_{N=0}^{\infty} \frac{1}{N! h^{DN}} \int d^{DN} r d^{DN} p \exp\left(-\tilde{\beta}\left(\sum_i \frac{p_i^2}{2m} - \mu N\right)\right), \end{aligned} \quad (4.9)$$

where the operator series $\widehat{\mathcal{D}}_2(d_\beta)$ appearing in (4.9) is

$$\widehat{\mathcal{D}}_2(d_\beta) = 1 - (1-q) \left(d_\beta^{(1)} + \frac{1}{2} d_\beta^{(2)}\right) + (1-q)^2 \left(d_\beta^{(2)} + \frac{5}{6} d_\beta^{(3)} + \frac{3}{8} d_\beta^{(4)}\right) + \dots \quad (4.10)$$

In the second step the phase space integral and the summation over the number of particles N is carried out in (4.9) and the resultant expression is

$$\mathfrak{c}^{(3)}(\mu, V, \beta) = \frac{1}{\left(\bar{Z}_q^{(3)}(\mu, V, \beta)\right)^q} \widehat{\mathcal{D}}_2(d_\beta) \exp(\mathcal{L}) Z_{BG}(\tilde{\beta}). \quad (4.11)$$

In the final step, the rhs in (4.11) is computed and the series corresponding to the generalized partition function (4.6) is substituted to obtain the perturbative series corresponding to the sum of q -weights

$$\mathfrak{c} = 1 + (1-q) \mathfrak{P}_1 + (1-q)^2 \mathfrak{P}_2 + \dots, \quad (4.12)$$

where the perturbative coefficients \mathfrak{P}_1 and \mathfrak{P}_2 are

$$\begin{aligned} \mathfrak{P}_1 &= -N_{BG}(\tilde{\beta}) (\alpha(\tilde{\beta}) - 1) \\ \mathfrak{P}_2 &= -\frac{1}{2} \mathcal{L} (\mathcal{L} - 1) + \frac{1}{2} (N_{BG}(\tilde{\beta}))^2 (2(\alpha(\tilde{\beta}))^3 + (\alpha(\tilde{\beta}))^2 + (2-D)\alpha(\tilde{\beta})) \\ &\quad + \frac{1}{4} N_{BG}(\tilde{\beta}) (2(\alpha(\tilde{\beta}))^3 + 2(2\mathcal{L} + 1)(\alpha(\tilde{\beta}))^2 + 6D\alpha(\tilde{\beta}) - (2\mathcal{L} - 1)(4 - D) + 4\mathcal{L}) \end{aligned} \quad (4.13)$$

The integral form of the grandcanonical heat function, the Hill energy $\mathbb{L}_q^{(3)}$ in the third constraint picture is

$$\begin{aligned} \mathbb{L}_q^{(3)}(\mu, V, \beta) &= \frac{1}{\left(\bar{Z}_q^{(3)}(\mu, V, \beta)\right)^q} \sum_{N=0}^{\infty} \frac{1}{N! h^{DN}} \int d^{DN} r d^{DN} p \left(\sum_i \frac{p_i^2}{2m} - \mu N\right) \times \\ &\times \left(\exp_q\left(-\tilde{\beta}\left(\sum_i \frac{p_i^2}{2m} - \mu N - \mathbb{L}_q^{(3)}\right)\right)\right)^q. \end{aligned} \quad (4.14)$$

Using a perturbative procedure akin to the one employed in the sum of q -weights the Hill energy in terms of the derivative series (4.10) is

$$\mathbb{L}_q^{(3)}(\mu, V, \beta) = \frac{1}{\left(\bar{Z}_q^{(3)}(\mu, V, \beta)\right)^q} \widehat{\mathcal{D}}_2(d_\beta) \left(\frac{D}{2\tilde{\beta}} - \mu\right) \exp(\mathcal{L}) N_{BG}(\tilde{\beta}) Z_{BG}(\tilde{\beta}). \quad (4.15)$$

Calculating the derivatives in the above expression and substituting the Boltzmann-Gibbs partition function, the perturbative series of the Hill energy upto $(1 - q)^2$ order is

$$\mathbf{L}_q^{(3)} = \mathbf{L}_{BG}(\tilde{\beta})(1 + (1 - q) \mathbf{L}_1 + (1 - q)^2 \mathbf{L}_2 + \dots). \quad (4.16)$$

where $\mathbf{L}_{BG}(\beta) = \left(\frac{D}{2\beta} - \mu\right) N_{BG}(\beta)$ and the coefficients of perturbation are listed below

$$\begin{aligned} \mathbf{L}_1 &= \alpha(\tilde{\beta}) + 2\mathcal{L} + (1 + \alpha(\tilde{\beta})) N_{BG}(\tilde{\beta}), \\ \mathbf{L}_2 &= -\frac{1}{8} (4(\alpha(\tilde{\beta}))^3 - 4(2 + D - 4(1 - D\mu) \tilde{\beta} - 4(\tilde{\beta}\mu)^2) \mathcal{L} + 4(3 + 4\tilde{\beta}\mu) \mathcal{L}^2 + 8 \\ &\quad + 2D \tilde{\beta}\mu - 8\tilde{\beta}^2) - \frac{1}{2} N_{BG}(\tilde{\beta}) (2 - D + 4D^2 \tilde{\beta}\mu - 8(\tilde{\beta}\mu)^2 - 6(\alpha(\tilde{\beta}))^3 + (3D \\ &\quad - 2D^2 + 8(1 - D) \tilde{\beta}\mu - 8(\tilde{\beta}\mu)^2) \mathcal{L}) - \frac{1}{8} (N_{BG}(\tilde{\beta}))^2 (3D^2 - 16D \tilde{\beta} + 20\tilde{\beta}^2 \\ &\quad - 16(\alpha(\tilde{\beta}))^3). \end{aligned} \quad (4.17)$$

From the perturbative solutions we notice that the generalized ensemble (4.6), the sum of q - weights (4.12) and the Hill energy (4.16) are coupled equations. The explicit expression corresponding to these quantities are obtained by employing a recursive procedure to solve these equations. The important characteristic feature that all these equations are uncoupled at $q = 1$ enables us to obtain a solution. Through the use of the recursive procedure, an explicit form of the generalized partition function is obtained up to second order in $(1 - q)$ and reads:

$$Z_q^{(3)}(\beta) = Z_{BG}(\beta)(1 + (1 - q) \mathcal{Z}_1(\beta) + (1 - q)^2 \mathcal{Z}_2(\beta) + \dots). \quad (4.18)$$

where the coefficients of perturbation are

$$\begin{aligned}
\mathcal{Z}_1(\beta) &= -\frac{1}{16}(4D + 4D^2 + D^3 - (4D - 2D^2)\beta\mu + (8 - 4D)(\beta\mu)^2 + 8(\beta\mu)^3)N_{BG}(\beta) \\
&\quad + \frac{1}{8}(4D + 4D^2 + D^3 - (8D + 4D^2)\beta\mu + 8(1 + D)(\beta\mu)^2 - 8(\beta\mu)^3)(N_{BG}(\beta))^2, \\
\mathcal{Z}_2(\beta) &= +\frac{1}{768}(32D + 88D^2 + 28D^3 + 2D^4 + 3D^5 - (32D + 168D^2 + 40D^3 \\
&\quad - 18D^4)\beta\mu + (96D + 96D^2 - 24D^3)(\beta\mu)^2 - (512 - 416D + 240D^3)(\beta\mu)^3 \\
&\quad - (544 - 432D)(\beta\mu)^4 - 96(\beta\mu)^5)N_{BG}(\beta) + \frac{1}{512}(176D^2 - 32D^4 + 8D^5 + D^6 \\
&\quad - (160D^2 - 432D^3 - 8D^4 - 4D^5)\beta\mu + (576D - 656D^2 - 160D^3 \\
&\quad + 12D^4)(\beta\mu)^2 - (1024 + 640D - 704D^2 + 32D^3)(\beta\mu)^3 - (704 + 1024D \\
&\quad - 48D^2)(\beta\mu)^4 + (384 - 64D)(\beta\mu)^5 + 64(\beta\mu)^6)(N_{BG}(\beta))^2 - \frac{1}{128}(32D \\
&\quad + 48D^2 + 16D^3 + 2D^5 + D^6 - (32D - 32D^2 - 96D^3 - 24D^4 + 6D^5)\beta\mu \\
&\quad + (192 - 64D - 208D^2 - 152D^3 - 20D^4)(\beta\mu)^2 - (320 - 128D - 368D^2 \\
&\quad + 48D^3)(\beta\mu)^3 - (128 + 448D - 80D^2)(\beta\mu)^4 + (192 - 96D)(\beta\mu)^5 \\
&\quad - 64(\beta\mu)^6)(N_{BG}(\beta))^3 + \frac{1}{128}(16D^2 + 32D^3 + 24D^4 + 8D^5 + D^6 - (64D^2 \\
&\quad + 96D^3 + 48D^4 + 8D^5)\beta\mu + (64D + 192D^2 + 144D^3 + 32D^4)(\beta\mu)^2 - (192D \\
&\quad + 256D^2 + 80D^3)(\beta\mu)^3 + (64 + 256D + 128D^2)(\beta\mu)^4 - 128(1 + D)(\beta\mu)^5 \\
&\quad + 64(\beta\mu)^6)(N_{BG}(\beta))^4. \tag{4.19}
\end{aligned}$$

A similar application of the recursive procedure enables us to calculate the explicit expression of the Hill energy upto second order in $(1 - q)$. The perturbative series corresponding to the Hill energy is

$$\mathbf{L}_q^{(3)}(\beta) = \mathbf{L}_{BG}(\beta) \left(1 + (1 - q) \mathbf{L}_1(\beta) + (1 - q)^2 \mathbf{L}_2(\beta) + \cdots \right), \tag{4.20}$$

and the coefficients of perturbation are listed below

$$\begin{aligned}
\mathbf{L}_1(\beta) &= -\left(\frac{1}{16} (D^3 + 2D^2 + 12D \beta\mu + 4D \beta\mu \alpha(\beta) + 16 (\beta\mu)^2 + 8(\beta\mu)^3) + \frac{1}{8} (4D \right. \\
&\quad \left. + 2D^2 + D^3 + 8D \beta\mu \alpha(\beta) + 8(\alpha(\beta))^2 - 8(\beta\mu)^3) N_{BG}(\beta)\right) U_{BG}(\beta), \\
\mathbf{L}_2(\beta) &= \left(\frac{1}{768} (16D^2 - 12D^3 - 4D^4 + 3D^5 - (32D + 72D^2 - 8D^3 - 18D^4) \beta\mu \right. \\
&\quad + (192D - 48D^2 - 24D^3) (\beta\mu)^2 - (768 - 608D - 240D^2) (\beta\mu)^3 - (640 \\
&\quad - 432D) (\beta\mu)^4 - 96 (\beta\mu)^5) + \frac{1}{16} (4D^2 - 2D^3 - (8D + 10D^2 - 13D^3) \beta\mu \\
&\quad + (32D - 18D^2 - 5D^3) (\beta\mu)^2 + 28D (\beta\mu)^4 + 8 (\beta\mu)^5) N_{BG}(\beta) + \frac{1}{64} (8D^2 \\
&\quad + 20D^3 + 14D^4 + 3D^5 - (16D + 56D^2 + 76D^3 + 26D^4) \beta\mu - (64 - 80D \\
&\quad - 128D^2 - 100D^3) (\beta\mu)^2 + (96 - 80D - 208D^2) (\beta\mu)^3 + (64 + 224D) (\beta\mu)^4 \\
&\quad \left. - 96(\beta\mu)^5) (N_{BG}(\beta))^2\right) U_{BG}(\beta). \tag{4.21}
\end{aligned}$$

The knowledge of the explicit form of the generalized partition function (4.18) and the Hill energy (4.20) enables us to compute the average number of particles and the internal energy. First the entropy of the system is calculated from the generalized partition function (4.18) through the use of (2.20). In the next step the explicit form of the Hill energy (4.20) is used in conjunction with the entropic expression in the relation $\Phi_q^{(3)} = \mathbf{L}_q^{(3)} - TS$ to obtain the free energy. From the free energy the average number of particles can be found through the use of a specific form of (2.22) i.e., $N_q^{(3)} = -\frac{\partial \Phi_q^{(3)}}{\partial \mu}$. The explicit expression corresponding to the average number of particles in the third constraint $N_q^{(3)}$ is

$$N_q^{(3)} = N_{BG}(\beta) + (1 - q) \mathfrak{N}_1(\beta) + (1 - q)^2 \mathfrak{N}_2(\beta) + \dots, \tag{4.22}$$

where the terms \mathfrak{N}_1 and \mathfrak{N}_2 are

$$\begin{aligned}
\mathfrak{N}_1(\beta) &= -\frac{1}{4} N_{BG}(\beta) ((2 \underline{()^2} + 4 \underline{-D}) - 4 N_{BG}(\beta) (\underline{()^2} - \underline{)}) \\
\mathfrak{N}_2(\beta) &= \frac{1}{96} N_{BG}(\beta) (12 \underline{()^4} + 80 \underline{()^3} + 12(8 - 7D)(\beta\mu)^2 - 6D^2(2 - D)^2 \beta\mu \\
&\quad + D(1 - D)(4 + D)) - \frac{1}{8} (N_{BG}(\beta))^2 (4 \underline{()^4} + 8 \underline{()^3} + 8D \underline{()^2} \\
&\quad - 16 \beta\mu \underline{-D}(4 + D)) + \frac{1}{16} (N_{BG}(\beta))^3 (24 \underline{()^4} - 16 \beta\mu(1 + \beta\mu) \underline{-} \\
&\quad - 8(1 - 8D)(\beta\mu)^2 + 8(2 - 3D^2)\beta\mu - D(4 - 2D - 5D^2)). \tag{4.23}
\end{aligned}$$

The calculated results corresponding to the Hill energy (4.20) and the average number of particles (4.22) is used in the relation $\mathbf{L}_q^{(3)} = U_q^{(3)} - \mu N_q^{(3)}$ to find the internal energy. The perturbative series corresponding to the internal energy is

$$U_q^{(3)}(\beta) = U_{BG}(\beta) + (1 - q) \mathcal{U}_1 + (1 - q)^2 \mathcal{U}_2 + \dots, \tag{4.24}$$

where the perturbative terms are listed below

$$\begin{aligned}
\mathcal{U}_1(\beta) &= -\frac{1}{2} ((\beta\mu)^2 - 2\beta\mu + D(2+D) + 2(D+2\beta\mu \\
&\quad - 2(1+D)) N_{BG}(\beta)) U_{BG}(\beta), \\
\mathcal{U}_2(\beta) &= \frac{1}{96} \left((12\beta\mu^4 + 48(\beta\mu)^4 - 16(\beta\mu)^3 + 36D(1-D)(\beta\mu)^2 + 12D(2-D^2)\beta\mu \right. \\
&\quad + D(4-3D-D^2)) - 4N_{BG}(\beta) (24(\beta\mu)^3 + 42D(\beta\mu)^2 - 88D^2\beta\mu \\
&\quad - 6D(1-D)(2+D) - (36(\beta\mu)^3 + 12D(\beta\mu)^2 + 3(16+D^2)\beta\mu)) \\
&\quad + 3(N_{BG}(\beta))^2 (32\beta\mu^4 + 4(8+D^2)\beta\mu + 16(\beta\mu)^3 + 32(5+2D)(\beta\mu)^2 \\
&\quad \left. - (32+32D-56D^2-2D^3)\beta\mu + D(8+20D+14D^2+D^3)) \right) U_{BG}(\beta) \quad (4.25)
\end{aligned}$$

The average number and the internal energy can also be calculated in a different manner wherein the basic definition of these quantities in (2.11,2.12) is used to find the implicit expressions. The implicit expressions are then solved to arrive at the final explicit forms. The results obtained through this method agrees precisely with those obtained with those in (4.22) and (4.24). This is a nontrivial consistency check on the results obtained for the physical quantities.

The entire calculation has been carried out directly in the third constraint picture and consistently upto second order in the expansion parameter $(1-q)$. However the process is not limited only to the second order and it can be extended to any arbitrary order in the expansion parameter.

B. Extreme relativistic classical ideal gas

The perturbative study carried out for the nonrelativistic classical ideal gas can also be extended to the system of extreme relativistic classical ideal gas. Since the calculational procedure is same as in the nonrelativistic case detailed in the previous section, we present only the final expressions corresponding to the internal energy and the average number of particles. The average number of particles is

$$N_q^{(3)}(\beta) = N_{BG}(\beta) + (1-q) N_1(\beta) + (1-q)^2 N_2(\beta) + \dots, \quad (4.26)$$

where the term $N_{BG} = \exp(\beta\mu) V \Delta \beta^{-D}$ and the coefficients of perturbation are

$$\begin{aligned}
N_1(\beta) &= -\frac{1}{2} N_{BG}(\beta) ((\beta\mu)^2 + 2(1+D)\beta\mu - D(1-D)) + (N_{BG}(\beta))^2 ((\beta\mu)^2 \\
&\quad - (2+D)\beta\mu + 3D-1), \\
N_2(\beta) &= -\frac{1}{24} N_{BG}(\beta) (3(\beta\mu)^4 + (20-12D)(\beta\mu)^3 + (24-42D)(\beta\mu)^2 \\
&\quad - 12D(1-2D-D^2)\beta\mu + 2D-3D^2-2D^3+3D^4 - \frac{1}{2} (N_{BG}(\beta))^2 ((\beta\mu)^4 \\
&\quad - 2D(\beta\mu)^3 - (8-10D)(\beta\mu)^2 - (6-12D+16D^2-2D^3)\beta\mu \\
&\quad - D^2(1-6D+D^2)) + \frac{1}{2} (N_{BG}(\beta))^3 (3(\beta\mu)^4 - (9-6D)(\beta\mu)^3 \\
&\quad - (2-28D-3D^2)(\beta\mu)^2 + (22-20D-19D^2)\beta\mu + 2-11D+20D^2+D^3). \quad (4.27)
\end{aligned}$$

The final expression for the internal energy is

$$\mathcal{U}_q^{(3)}(\beta) = \mathcal{U}_{BG}(\beta) + (1-q) \mathcal{U}_1(\beta) + (1-q)^2 \mathcal{U}_2(\beta) + \dots, \quad (4.28)$$

and the coefficients of perturbation are listed below

$$\begin{aligned} \mathcal{U}_1(\beta) &= -((\beta\mu)^2 - 2D\beta\mu + D(1+D))\mathcal{U}_{BG}(\beta) + \mathcal{N}_{BG}(\beta)((\beta\mu)^2 - (3+D)\beta\mu \\ &\quad + (1+3D))\mathcal{U}_{BG}(\beta), \\ \mathcal{U}_2(\beta) &= \left(\frac{1}{24} (3(\beta\mu)^4 + (8-12D)(\beta\mu)^3 - 6D(1+3D)(\beta\mu)^2 - 12D^2(D+1)\beta\mu \right. \\ &\quad + 2D + 6D^2 + 10D^3 + 3D^4) - \frac{1}{2} \mathcal{N}_{BG}(\beta)((\beta\mu)^4 - 2(1+D)(\beta\mu)^3 \\ &\quad - (4-2D)(\beta\mu)^2 - (4D+14D^2-2D^3)\beta\mu + 2D + 7D^2 - 4D^3 + 2D^4) \\ &\quad + \frac{1}{2} (\mathcal{N}_{BG}(\beta))^2 (3(\beta\mu)^4 + (13-6D)(\beta\mu)^3 + (13-32D+3D^2)(\beta\mu)^2 \\ &\quad \left. - (1+40D+19D^2)\beta\mu + 1 + 9D + 21D^2 + D^2) \right) \mathcal{U}_{BG}(\beta). \end{aligned} \quad (4.29)$$

and the Boltzmann-Gibbs factor is $\mathcal{U}_{BG} = \frac{D}{\beta} \mathcal{N}_{BG}$. The Boltzmann-Gibbs values for both the quantities are recovered in the $q \rightarrow 1$ limit.

The thermodynamic results corresponding to a one dimensional model of an interacting gas known as Tonks gas described by the Hamiltonian (3.36) can be read from the results of the classical nonrelativistic ideal gas. For this purpose we employ a special kind of grandcanonical ensemble where the free length or the total length available to the molecules is used instead of volume. Also the number of dimensions is set to be 1 and the factor \mathcal{M}_1 the one dimensional analog of \mathcal{M} is used.

V Generalized ensemble

The generalized ensemble describes a completely open system which can exchange the internal energy, the volume and the number of particles. The heat function is the \mathcal{R} function described by $\mathcal{R} = U + PV - \mu N$ and the generalized free energy is the function $\mathcal{E} = U - TS + PV - \mu N$.

A. Nonrelativistic ideal gas

The classical nonrelativistic ideal gas is analyzed in the generalized ensemble picture. A perturbative process based on the idea of disentangling of q -exponential [22] is used. Though the thermodynamic quantities are evaluated uniformly up to $(1-q)^2$ order, the results are presented only up to the first order in $(1-q)$ since some of the quantities are too cumbersome to be displayed up to second order. The generalized partition function in the third constraint picture is

$$\bar{\Upsilon}_q^{(3)}(\mu, V, \beta) = \sum_{N=0}^{\infty} \frac{1}{N! h^{DN}} \int d^{DN} r d^{DN} p \exp_q \left(-\hat{\beta} \left(\sum_i \frac{p_i^2}{2m} + PV - \mu N - \mathcal{R}_q^{(3)} \right) \right), \quad (5.1)$$

where the factor $\hat{\beta} = \frac{\beta}{\mathfrak{c}^{(3)}}$ and $\mathfrak{c}^{(3)}$ is the third constraint sum of q -weights in the generalized ensemble. The heat function $\mathbf{R}_q^{(3)} = U_q^{(3)} + PV_q^{(3)} - TS - \mu N_q^{(3)}$ where $U_q^{(3)}$, $V_q^{(3)}$, and $N_q^{(3)}$ are the internal energy, average volume and average number of particles respectively in the third constraint. The quantities P and μ denote the pressure and the chemical potential of the system.

In (5.1) the phase space integrals can be carried out after the due substitution of the perturbative expansion of the q -exponential in terms of the ordinary exponential. Since the volume states are very close to each other, we approximate the volume summation by an integral. Employing the correct counting of volume states advocated in [25,26], we carry out the volume integral. Finally we assume that the summation over the number of particles is convergent atleast, in the neighbourhood of $q = 1$ and, thus arrive at the final perturbative series of the generalized partition function

$$\bar{\Upsilon}_q^{(3)}(\mu, P, \beta) = \hat{\mathcal{D}}_1(d_\beta) \exp(\mathcal{R}) \Upsilon_{BG}(\hat{\beta}), \quad (5.2)$$

where $\mathcal{R} = \hat{\beta} \mathbf{R}_q^{(3)}$ and $\hat{\mathcal{D}}_1(d_\beta)$ is the derivative series defined in (4.4). The partition function and the average number of particles in the Boltzmann-Gibbs framework is

$$\Upsilon_{BG}(\beta) = \frac{1}{1 - \omega(\beta)}, \quad N_{BG}(\beta) = \frac{\omega(\beta)}{1 - \omega(\beta)}, \quad \omega(\beta) = \exp(\beta\mu) \mathcal{M} \frac{1}{P} \left(\frac{1}{\beta} \right)^{\frac{D}{2}+1}, \quad (5.3)$$

where the factor $\omega(\beta)$ is considered to be less than 1 so as to maintain the positivity of the partition function. From (5.2) the perturbative series corresponding to the third constraint generalized partition function upto $(1 - q)$ order is computed

$$\begin{aligned} \bar{\Upsilon}_q^{(3)}(\mu, P, \beta) = & \exp(\mathcal{R}) \Upsilon_{BG}(\hat{\beta}) \left(1 + (1 - q) \frac{1}{4} \left((2(\alpha(\hat{\beta}))^2 + 4R\hat{\beta}\alpha(\hat{\beta}) - 4(R + \mu)\hat{\beta} \right. \right. \\ & \left. \left. + (4 + 3D))N_{BG}(\hat{\beta}) + (2(\alpha(\hat{\beta}))^2 - 4\alpha(\hat{\beta}) + 2)(N_{BG}(\hat{\beta}))^2 \right) + \dots \right). \end{aligned} \quad (5.4)$$

Applying a similar perturbative technique, the sum of q -weights in the generalized ensemble picture reads:

$$\mathfrak{c}^{(3)}(\mu, P, \beta) = \frac{1}{\left(\bar{\Upsilon}_q^{(3)}(\mu, P, \beta) \right)^q} \hat{\mathcal{D}}_2(d_\beta) \exp(\mathcal{R}) \Upsilon_{BG}(\hat{\beta}), \quad (5.5)$$

where the derivative series $\hat{\mathcal{D}}_2(d_\beta)$ is defined in (4.10). Employing the derivative series, the perturbative expression of the sum of q -weights upto first order in $(1 - q)$ is

$$\mathfrak{c}^{(3)}(\hat{\beta}) = 1 + (1 - q) \left(((\alpha(\hat{\beta}) + 1) - \Upsilon_{BG}(\hat{\beta})) \omega(\hat{\beta}) - \Upsilon_{BG}(\hat{\beta}) \right) \ln \Upsilon_{BG}(\hat{\beta}) + \dots \quad (5.6)$$

Adopting a procedure identical to the one used for the generalized partition function and the sum of q -weights, the $\mathbf{R}_q^{(3)}$ heat function can be written as:

$$\mathbf{R}_q^{(3)}(\mu, P, \beta) = \frac{1}{\left(\bar{\Upsilon}_q^{(3)}(\mu, P, \beta) \right)^q} \hat{\mathcal{D}}_2(d_\beta) \left(\left(\frac{D}{2} + 1 \right) \frac{1}{\hat{\beta}} - \mu \right) \exp(\mathcal{R}) N_{BG}(\hat{\beta}) \Upsilon_{BG}(\hat{\beta}). \quad (5.7)$$

The perturbative series of the $R_q^{(3)}$ upto $(1 - q)$ order found from (5.7) is

$$R_q^{(3)}(\mu, P, \beta) = \left(\left(\frac{D}{2} + 1 \right) \frac{1}{\hat{\beta}} - \mu \right) N_{BG}(\hat{\beta}) + (1 - q) (R_1 + R_2 + R_3) + \dots \quad (5.8)$$

The perturbative coefficients of $(1 - q)$ term in (5.8) is

$$\begin{aligned} R_1 &= \left(R^2 \hat{\beta} (1 - \alpha(\hat{\beta})) + \frac{1}{16} \left((4(D+2)(D+4) P^{-1} \hat{\beta}^{-2} - (D+2)((D+4)(D+6) \right. \right. \\ &\quad + 8(R+2\mu)P^{-1}) \hat{\beta}^{-1} + (R+\mu) \mu P^{-1} + 3\mu - 4((D+2)(R+4\mu)R \\ &\quad - (2R^2 - 6\mu - 3D\mu)\mu) + 6D(D+6)\mu + 8(R+\mu)(\hat{\beta}\mu)^2) \\ &\quad + \omega(\hat{\beta}) (2(D^3 + 40D^2 + 32D + 32 + 2(D+2)R^2 + 4(D+2)(R+2\mu)) P^{-1} \hat{\beta}^{-1} \\ &\quad - 4(D+2)(D+4)P^{-1} \hat{\beta}^{-2} - 4(2(D^2 + 5D + 3)R + (D+2)(3D+10)\mu \\ &\quad + 4(R+\mu)\mu P^{-1}) + 8((2D+4)R + 3D\mu) \hat{\beta}\mu - ((R+2\mu)^2 \\ &\quad \left. \left. - 2\mu^2)(\hat{\beta}\mu)^2) \right) \Upsilon_{BG}(\hat{\beta}) \right) N_{BG}(\hat{\beta}), \\ R_2 &= \frac{1}{8} \left((D+2)^3 \hat{\beta}^{-1} + (D+2)((D+2)(3D+8) + 12\mu^2) - 2(12\mu^3 P^2 + 4\mu^3 P^{-1} \right. \\ &\quad + 4(9D^2 + 34D + 32)\mu P^2 + 2(D+2)^2 R P^2) \hat{\beta}^2 + 4((9D+14)\mu^2 \\ &\quad + 2(D+2)R\mu P^2) \hat{\beta}^3 - 12(D+2)^2 \mu - ((3D^3 + 20D^2 + 44D + 32) P^2 \hat{\beta} \\ &\quad - 2((9D^2 + 34D + 32)\mu + 2(D+2)^2 R) \hat{\beta} P^2 - 4(4(D+2)R \\ &\quad + (9D+14)\mu) P^2 \hat{\beta}^3 \mu + (2R+3\mu) \hat{\beta}^5 \mu^3 P^2) \Upsilon_{BG}(\hat{\beta}) (N_{BG}(\hat{\beta}))^2, \\ R_3 &= \frac{1}{8} \left(3\omega(\hat{\beta})((D+2)^3 P^3 \hat{\beta}^2 - 6(D+2)^2 \mu P^3 \hat{\beta}^3 + 12(D+2)\mu^2 \hat{\beta}^4 P^3 - 8\mu^3 \hat{\beta}^5 P^3) \right. \\ &\quad - 3((D+2)^3 \hat{\beta}^2 P^3 - 6(D+2)^2 \mu \hat{\beta}^3 P^3 + 12(D+2)\hat{\beta}^4 \mu^2 P^3 \\ &\quad \left. - 8\hat{\beta}^5 \mu^3 P^3) \right) \Upsilon_{BG}(\hat{\beta}) (N_{BG}(\hat{\beta}))^3. \end{aligned} \quad (5.9)$$

The generalized partition function (5.4), the sum of q -weights (5.6), and the $R_q^{(3)}$ heat function (5.8), form a set of coupled implicit perturbative expansions. The fact that these equations are uncoupled at the lowest perturbative order allows us to obtain an explicit form of these quantities through the use of a recursive procedure. The final explicit form of the generalized partition function computed upto first order in the expansion parameter $(1 - q)$ is

$$\bar{\Upsilon}_q^{(3)}(\beta) = \Upsilon_{BG}(\beta) \exp(\beta R) (1 + (1 - q)(\Upsilon_1(\beta) + \Upsilon_2(\beta) + \Upsilon_3(\beta) + \Upsilon_4(\beta)) + \dots), \quad (5.10)$$

and the coefficients of perturbation are listed below:

$$\begin{aligned}
\Upsilon_1(\beta) &= -\frac{1}{16} \left(4(2(\alpha(\beta))^2 - 4\alpha(\beta) + D) - ((2+D) \frac{1}{\beta P} ((2+D)(4+D - \beta\mu) \right. \\
&\quad \left. - 4(\beta\mu)^2) - 4(4+6D+D^2+2(2+D)\beta\mu) \ln \Upsilon_{BG}(\beta) \right) \Upsilon_{BG}(\beta) \\
&\quad + 2(D(2+D)\beta\mu - 4(\beta\mu)^3 - 4(2(2+D) - 2(1-D)\beta\mu \\
&\quad \left. - (\beta\mu)^2) \ln \Upsilon_{BG}(\beta) \right) (\Upsilon_{BG}(\beta))^2 + 16 \frac{1}{(\beta P)^2} (1 + \alpha(\beta)) (\Upsilon_{BG}(\beta))^3 \Big) N_{BG}(\beta), \\
\Upsilon_2(\beta) &= -\frac{1}{8} \left((6+3D - (8+D)\beta\mu - (\beta\mu)^2 - 2(1+D - \beta\mu) \ln \Upsilon_{BG}(\beta)) \right. \\
&\quad \left. + (16+8D-2D^2-16\beta P - (8-10D+D^2+8\beta P-4D\beta P)\beta\mu \right. \\
&\quad \left. - (8+4D+8\beta P)(\beta\mu)^2 + 12(\beta\mu)^3 + 4(6+3D-2(\beta P)^{-1} - (4-D)\beta\mu \right. \\
&\quad \left. + (\beta\mu)^2) \ln \Upsilon_{BG}(\beta) \right) \Upsilon_{BG}(\beta) - 4((\beta P)^{-2} - 4(\beta P)^{-1}\alpha(\beta) \\
&\quad \left. - (\alpha(\beta))^2) (\Upsilon_{BG}(\beta))^2 \right) (N_{BG}(\beta))^2, \\
\Upsilon_3(\beta) &= -\frac{(\Upsilon_{BG}(\beta))^3}{\beta P} \ln \Upsilon_{BG}(\beta) - \frac{1}{4} (8+6D+D^2 - (16+4D+4\beta P)\beta\mu \\
&\quad + 12(\beta\mu)^2 + 4(1-\alpha(\beta)) \ln \Upsilon_{BG}(\beta) + 4(\alpha(\beta))^2 + (\beta P)^{-1}\alpha(\beta)) (N_{BG}(\beta))^3, \\
\Upsilon_4(\beta) &= -\frac{1}{2} (\alpha(\beta))^2 (N_{BG}(\beta))^4. \tag{5.11}
\end{aligned}$$

Proceeding similarly the final explicit form of the heat function $R_q^{(3)}$ is obtained upto $(1-q)$ order

$$R_q^{(3)} = \left(\left(\frac{D}{2} + 1 \right) \frac{1}{\beta} - \mu \right) + (1-q) (R_1 + R_2 + R_3) + \dots, \tag{5.12}$$

where the perturbative coefficients may be listed as

$$\begin{aligned}
R_1 &= \frac{1}{4} \left((D+2)(D+4)\beta^{-1} - (D+2)\mu - \beta\mu^2 \right) (\Upsilon_{BG}(\beta))^2 \ln \Upsilon_{BG}(\beta) N_{BG}(\beta), \\
R_2 &= -\frac{1}{16} \left(\left((D+2)(3D+10)P - (D+2)(3\mu - (D^2-10D-40)P)P\beta \right. \right. \\
&\quad \left. \left. + 2(24\mu - (D+2)(3D-16)P)\mu P\beta^2 + 4(3D-20)\mu^2 P^2\beta^3 - 8\mu^3 P^2\beta^4 \right. \right. \\
&\quad \left. \left. + 2(8\mu - 3(D+2)(D+4)P)\beta\mu + 12(D+2)P(\beta\mu)^2 - 8P(\beta\mu)^3 \right. \right. \\
&\quad \left. \left. - (D+2)(16\mu + (D+4)(D+6)P) \right) \Upsilon_{BG}(\beta) - 2 \left((D+2)^2(D+4)\beta^{-1} \right. \right. \\
&\quad \left. \left. - 2(D+2)(3D+8)\mu^2 + 12(D+2)\beta\mu^2 - 8\beta^2\mu^3 + 2((D+2)^2\beta^{-1} \right. \right. \\
&\quad \left. \left. - 4(D+2)\mu + 4\beta\mu^2) \ln \Upsilon_{BG}(\beta) \right) (\Upsilon_{BG}(\beta))^2 \right) (N_{BG}(\beta))^2, \\
R_3 &= \frac{1}{8} \left(2(D+2)((9D+10)\mu + 2(D^2+3D+1)P)P^2\beta^2 - D(D+2)(3D+8)P^2\beta \right. \\
&\quad \left. - 4((9D+14)\mu + (D+2)(3D+4)P^2)\mu\beta^3 + 8(3\mu + 2(3D+5)P)\mu^2 P^2\beta^4 \right. \\
&\quad \left. - 2P^3\mu^3\beta^5 \right) (N_{BG}(\beta))^3. \tag{5.13}
\end{aligned}$$

To compute the other thermodynamic quantities like the internal energy, average volume and the average number of particles we need to calculate the free energy via the expression $\mathcal{E}_q^{(3)} = U_q^{(3)} + PV_q^{(3)} - TS - \mu N_q^{(3)} = R_q^{(3)} - TS$. The entropy which can be read from the generalized partition function (5.10) using the relation (2.20), and the perturbative expansion of the heat function $R_q^{(3)}$ are used in this process. From the free energy, the average volume can be found through the use of the thermodynamic relation $V_q^{(3)} = \frac{\partial \mathcal{E}_q^{(3)}}{\partial P}$. The perturbative expansion of the average volume upto $(1 - q)$ order is

$$\begin{aligned} V_q^{(3)} = & V_{BG}(\beta) + (1 - q) \frac{1}{4} \left(2 (\alpha(\beta))^2 - 2 \alpha(\beta) + 4 + D + 3(2 (\alpha(\beta))^2 - 4 \alpha(\beta) \right. \\ & + 8 + D) \Upsilon_{BG}(\beta) + 4 ((\omega(\beta))^2 + (\alpha(\beta) - 3) \omega(\beta) - (\alpha(\beta) - 2)) \ln \Upsilon_{BG}(\beta) \\ & \left. + \omega(\beta) (1 + \omega(\beta)) ((\alpha(\beta))^2 - \alpha(\beta) + 2) \right) V_{BG}(\beta) + \dots, \end{aligned} \quad (5.14)$$

where $V_{BG}(\beta)$ is the average volume in the Boltzmann-Gibbs formalism. Similarly the average number of particles can be arrived through the use of the relation $N_q^{(3)} = \frac{\partial \mathcal{E}_q^{(3)}}{\partial \mu}$. The final expression of the average number as a perturbative series upto first order in $(1 - q)$ is

$$\begin{aligned} N_q^{(3)} = & N_{BG}(\beta) + (1 - q) \frac{1}{8} \left((4 (\beta\mu)^2 + 8 \beta P \alpha(\beta) - D(2 + D) + 8 (\alpha(\beta) \right. \\ & + 1) \ln \Upsilon_{BG}(\beta)) N_{BG}(\beta) - (12 (\beta\mu)^2 - 4D \beta\mu - 8 \beta P (\alpha(\beta) + 1) - D(2 + D) \\ & \left. + 8 (\alpha(\beta) - 1) \ln \Upsilon_{BG}(\beta)) (N_{BG}(\beta))^2 + 4 (2 \beta\mu - \beta P - 1) (N_{BG}(\beta))^3 \right) + \dots. \end{aligned} \quad (5.15)$$

Using the perturbative expansions of the heat function (5.12), the average volume (5.14) and the average number of particles (5.15), the internal energy can be computed via the legendre transformation $R_q^{(3)} = U_q^{(3)} + PV_q^{(3)} - \mu N_q^{(3)}$. The computed perturbative series of the internal energy upto $(1 - q)$ order reads:

$$\begin{aligned} U_q^{(3)} = & U_{BG}(\beta) - (1 - q) \frac{1}{8} \Upsilon_{BG}(\beta) ((8 \ln \Upsilon_{BG}(\beta) + \alpha(\beta) - 1) \omega(\beta) + 8 (\alpha(\beta) \\ & - 2) \ln \Upsilon_{BG}(\beta) + 4 (\beta\mu - 2) \alpha(\beta) + 2D \beta\mu - (D + 1)^2) U_{BG}(\beta) + \dots. \end{aligned} \quad (5.16)$$

The quantities evaluated above can also be arrived at using the basic definition of the internal energy, the average volume and the average number of particles. For this purpose we employ the basic definition of these quantities to find the corresponding implicit equations which are then solved recursively to obtain the final explicit expressions. The results obtained through this method perfectly agrees with the results displayed above. All the quantities recover the corresponding Boltzmann-Gibbs results in the $q \rightarrow 1$ limit.

B. Extreme relativistic ideal gas

The extreme relativistic ideal gas has been studied using the perturbative formalism. The actual process of calculation is same as in the nonrelativistic case and so we present

the final results directly. The perturbative expansion corresponding to the the average number of particles is

$$\begin{aligned} \mathbb{N}_q^{(3)} = \mathbb{N}_{BG} - \frac{(1-q)}{2} \Upsilon_{BG}(\beta) \left(D + D^2 - 2D\beta\mu + (\beta\mu)^2 \right. \\ \left. - 2(1 + D - \beta\mu) \ln \Upsilon_{BG}(\beta) \right) \mathbb{N}_{BG}(\beta) + \dots \end{aligned} \quad (5.17)$$

The factors $\Upsilon_{BG}(\beta)$ and $\mathbb{N}_{BG}(\beta)$, are the partition function and average number in the Boltzmann-Gibbs statistics respectively and their expressions are given below

$$\Upsilon_{BG}(\beta) = \frac{1}{1 - \xi(\beta)}, \quad \mathbb{N}_{BG} = \frac{\xi(\beta)}{1 - \xi(\beta)}, \quad \xi(\beta) = \exp(\beta\mu) \Delta \frac{1}{P} \left(\frac{1}{\beta} \right)^{D+1} \quad (5.18)$$

is the average number in the Boltzmann-Gibbs statistics and $\xi(\beta)$ is assumed to be less than 1. The average volume in nonextensive statistical mechanics is

$$\begin{aligned} \mathbb{V}_q^{(3)} = \mathbb{V}_{BG} - \frac{(1-q)}{2} \Upsilon_{BG}(\beta) \left((2 + 3D + D^2 - 2(1 + D)\beta\mu - (\beta\mu)^2 \right. \\ \left. - 2(2 + D - \beta\mu) \ln \Upsilon_{BG}(\beta) \right) \mathbb{V}_{BG}(\beta) - 2(1 + D - \beta\mu - \ln \Upsilon_{BG}(\beta)) (\mathbb{V}_{BG}(\beta))^2 + \dots \end{aligned} \quad (5.19)$$

where the Boltzmann-Gibbs value corresponding to it is $\mathbb{V}_{BG} = \frac{1}{\beta P} \mathbb{N}_{BG}(\beta)$. A similar perturbative series corresponding to the internal energy is

$$\begin{aligned} \mathbb{U}_q^{(3)} = \mathbb{U}_{BG} - \frac{(1-q)}{2} \Upsilon_{BG}(\beta) \left((2 + 3D + D^2 - (1 + D)\beta\mu - (\beta\mu)^2 \right. \\ \left. - 2(2 + D - \beta\mu) \ln \Upsilon_{BG}(\beta) \right) \mathbb{U}_{BG}(\beta) - 2(1 + D - \beta\mu - \ln \Upsilon_{BG}(\beta)) (\mathbb{U}_{BG}(\beta))^2 + \dots \end{aligned} \quad (5.20)$$

The Boltzmann-Gibbs internal energy used in (5.21) is $\mathbb{U}_{BG}(\beta) = \frac{D}{\beta} \mathbb{N}_{BG}(\beta)$. From the results displayed above we can observe that in the $q \rightarrow 1$ limit we recover the standard Boltzmann-Gibbs values.

The Tonks gas described by the Hamiltonian (3.36) can also be studied through the generalized ensemble. The results corresponding to such a model of interacting gas in the free length generalized ensemble can be obtained by substituting $D = 1$ in the results obtained for the nonrelativistic classical ideal gas.

VI Adiabatic ensemble

The adiabatic class of ensembles is used to describe a system of particles for which the thermal equilibration is with respect to the heat function. In the adiabatic class the individual members of the ensemble have the same value of the heat function though they can be at different temperatures. There are four different adiabatic ensembles namely microcanonical (N, V, U), isoenthalpic-isobaric ensemble (N, P, H), the ensemble with number fluctuations (μ, V, L), and the ensemble with both the number and volume fluctuations (μ, P, R). In the current section we present a unified framework to describe the adiabatic class of ensembles.

At any given instant in time the microstate of a system consisting of N particles is represented by a point in the $6N$ dimensional phase space, which is comprised of $3N$ position coordinates and the $3N$ momentum coordinates. Since the position and momentum coordinates evolve with time, the representative point moves in the phase space. The motion of the representative point traces a trajectory of constant heat function \mathfrak{H} in the phase space. The points which lie on the surface of the constant heat function curve are the various microstates corresponding to the macrostate of constant heat function. As the number of microstates is very high and lie very close to each other, the surface area of the constant heat function curve can be considered as a measure of the total number of microstates. The surface area of the constant heat function \mathfrak{H} curve in an adiabatic ensemble is

$$\Omega(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}) = \sum_{X_{\{\ell\}}} \frac{1}{N! h^{DN}} \int_{r_i} \int_{p_i} \delta\left(\mathcal{H} + \sum_{\{\ell\}} x_\ell X_\ell - \mathfrak{H}\right) \prod_{i=1}^N d^D r_i d^D p_i. \quad (6.1)$$

The computation of area of the constant heat function is difficult, and so we usually calculate the volume enclosed by such curve. The phase space volume enclosed by the constant heat function \mathfrak{H} curve is

$$\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}) = \sum_{X_{\{\ell\}}} \frac{1}{N! h^{DN}} \int_{r_i} \int_{p_i} \Theta\left(\mathcal{H} + \sum_{\{\ell\}} x_\ell X_\ell - \mathfrak{H}\right) \prod_{i=1}^N d^D r_i d^D p_i. \quad (6.2)$$

The surface area of the heat function curve (6.1) and the volume (6.2) enclosed by it are related via the relation

$$\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}) = \frac{\partial}{\partial \mathfrak{H}} \Omega(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}). \quad (6.3)$$

Based on the kind of adiabatic confinement there are four different definitions of the entropy. A unified definition of the entropy for an adiabatic nonextensive system is

$$S_q(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}) = k \ln_q \Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}), \quad (6.4)$$

where the $\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H})$ is the volume enclosed by the curve of constant heat function and a measure of the number of microstates. The temperature of a general adiabatic ensemble is defined via the relation

$$T = \left(\frac{\partial S_q}{\partial \mathfrak{H}} \right)^{-1} = \frac{(\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}))^q}{k \Omega(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H})}. \quad (6.5)$$

In the usual procedure of calculation the heat function can be computed through the use of (6.5) and the relations (6.1) and (6.2). Using the heat function the specific heat can be calculated through the expression

$$C_q|_{x_{\{\ell\}}} = \left. \frac{\partial \mathfrak{H}_q}{\partial T} \right|_{x_{\{\ell\}}}. \quad (6.6)$$

The extensive thermodynamic variable whose intensive counterparts are held fixed can be obtained from the relation

$$X_{\ell,q}(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}) = -\frac{1}{\beta} \frac{\partial}{\partial x_\ell} S_q(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}). \quad (6.7)$$

The volume and the average number of particles can be calculated in the (N, P, H) and (μ, V, L) respectively through the use of (6.7). In the case of (μ, P, R) ensemble, both the volume and the average number of particles can be calculated using (6.7). The expectation value of an observable O for any adiabatic ensemble can be defined in a unified way through the relation

$$\langle O \rangle = \frac{1}{\Omega(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H})} \sum_{X_{\{\ell\}}} \frac{1}{N! h^{DN}} \int_{r_i} \int_{p_i} O \delta\left(\mathcal{H} + \sum_{\{\ell\}} x_\ell X_\ell - \mathfrak{H}\right) \prod_{i=1}^N d^D r_i d^D p_i. \quad (6.8)$$

The internal energy is the natural heat function of the microcanonical ensemble and so it can be directly evaluated, whereas in the other three ensembles, equation (6.8) is used to calculate the internal energy. From the internal energy the specific heat at constant volume can be evaluated using

$$C_q|_V = \left. \frac{\partial U_q}{\partial T} \right|_V. \quad (6.9)$$

A nontrivial way of checking the internal energy can be accomplished by using the Legendre transform (1.3) to find the internal energy.

A q generalization of the equipartition theorem is developed in the unified framework. Let y_i be a phase space variable which can denote either the position r_i or the momentum p_i ($i = 1, \dots, 3N$) coordinate. Calculating the expectation value of $y_i \frac{\partial \mathcal{H}}{\partial y_j}$ we arrive at

$$\left\langle y_i \frac{\partial \mathcal{H}}{\partial y_j} \right\rangle = kT (\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}))^{q-1} \delta_{ij}. \quad (6.10)$$

Equation (6.10) obtained above is the generalized form of the q -nonextensive equipartition theorem. It is interesting to note that the nonextensive generalization of the equipartition theorem depends on the factor $\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H})$ which is a measure of the number of microstates corresponding to a given macrostate. However we notice that in the extensive $q \rightarrow 1$ limit the dependence on the number of microstates vanishes. The form of (6.10) suggests that the expectation value described has a nonzero value only when $i = j$. When the phase space variable y_i is set to be the coordinate r_i then we get a specific form of the equipartition theorem

$$\left\langle r_i \frac{\partial \mathcal{H}}{\partial r_i} \right\rangle = -\langle r_i \dot{p}_i \rangle = \langle r_i F_i \rangle = kT (\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}))^{q-1}, \quad (6.11)$$

where we have used Hamilton's equation of motion $\frac{\partial \mathcal{H}}{\partial r_i} = -\dot{p}_i$. Following an identical approach for the situation where the generalized variable is set to be the momentum variable $y_i = p_i$ we arrive at

$$\left\langle p_i \frac{\partial \mathcal{H}}{\partial p_i} \right\rangle = \langle p_i \dot{q}_i \rangle = kT (\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}))^{q-1}. \quad (6.12)$$

We observe that (6.12) is nothing but twice the expectation value of kinetic energy. From (6.11) and (6.12) it can be proved that systems whose Hamiltonians can be cast in the

form $\mathcal{H} = \sum_i A_i P_i^2 + \sum_i B_i Q_i^2$ through a canonical transformation the expectation value of the Hamiltonian is

$$\mathcal{H} = \frac{DN}{2} kT (\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}))^{q-1}. \quad (6.13)$$

The virial theorem in the nonextensive framework obtained from (6.11) reads:

$$\left\langle \sum_i^{3N} q_i \dot{p}_i \right\rangle = -3N kT (\Sigma(\mathfrak{X}_1, \mathfrak{X}_2, \mathfrak{H}))^{q-1}. \quad (6.14)$$

The unified framework derived above is made use of in the following sections to demonstrate the isenthalpic-isobaric ensemble (N, P, H) , the ensemble with number fluctuations (μ, V, L) and the ensemble with both number and volume fluctuations (μ, P, R) . Though all the relations in the microcanonical ensemble (N, V, U) can be read from the equations in the unified framework above, we do not discuss the (N, V, U) ensemble, since a detailed study has already been carried out in [21].

VII Isoenthalpic-Isobaric ensemble

The study of adiabatically confined systems with constant enthalpy is done using the Isoenthalpic-Isobaric ensemble. In the following discussion we study the classical nonrelativistic and extreme relativistic ideal gas.

A. Nonrelativistic ideal gas in (N, P, H) ensemble

The nonrelativistic ideal gas is studied in the isoenthalpic-isobaric ensemble. The volume enclosed by the surface of constant enthalpy is calculated in the following manner. First the Hamiltonian corresponding to the nonrelativistic gas (3.1) is substituted in equation (6.2) and the resultant expression reads:

$$\Sigma(N, P, H) = \sum_V \frac{1}{N! h^{DN}} \int_{r_i} \int_{p_i} \Theta \left(\sum_i \frac{p_i^2}{2m} + PV - H \right) \prod_{i=1}^N d^D r_i d^D p_i. \quad (7.1)$$

The momentum integration in (7.1) is geometrically the volume of DN dimensional sphere of radius $\sqrt{2m(H - PV)}$ and is equal to

$$_{nr} \mathcal{I}_p = \int_{\sum_i^{DN} \frac{p_i^2}{2m} \leq H - PV} d^{DN} p_i = \frac{(2\pi m)^{\frac{DN}{2}}}{\Gamma(\frac{DN}{2} + 1)} (H - PV)^{\frac{DN}{2}}. \quad (7.2)$$

Substituting the result of the momentum integration (7.2) in (7.1) the expression for the volume is

$$\Sigma(N, P, H) = \frac{\mathcal{M}^N}{N!} \frac{1}{\Gamma(\frac{DN}{2} + 1)} \sum_V (H - PV)^{\frac{DN}{2}} \int d^{DN} r_i. \quad (7.3)$$

In the next step the integral over the position coordinates is carried out in (7.3) and this yields

$$\Sigma(N, P, H) = \frac{\mathcal{M}^N}{N!} \frac{1}{\Gamma(\frac{DN}{2} + 1)} \sum_V V^N (H - PV)^{\frac{DN}{2}}. \quad (7.4)$$

Finally the summation over the volume eigenstates is considered. Since the volume states are very closely spaced the summation is approximated by an integral. But as we have discussed earlier an integration leads to overcounting of volume states. To overcome this we employ the shell particle method of counting of volume states proposed in [25,26], wherein only the distinct minimum volume states needed to confine the particle is taken into account. The volume enclosed by the isoenthalpic curve in phase space is

$$\Sigma(N, P, H) = \mathcal{M}^N \left(\frac{1}{P} \right)^N \frac{H^{\mathfrak{D}_1}}{\Gamma(\mathfrak{D}_1 + 1)} \quad (7.5)$$

The surface area of the constant enthalpy curve in the phase space is

$$\Omega(N, P, H) = \mathcal{M}^N \left(\frac{1}{P} \right)^N \frac{H^{\mathfrak{D}_1 - 1}}{\Gamma(\mathfrak{D}_1)} \quad (7.6)$$

From the volume of the isoenthalpic curve in the phase space the nonextensive entropy of the classical ideal gas in this ensemble is

$$S_q(N, P, H) = k \left(\frac{\left(\mathcal{M}^N \left(\frac{1}{P} \right)^N \frac{H^{\mathfrak{D}_1}}{\Gamma(\mathfrak{D}_1 + 1)} \right)^{1-q} - 1}{1 - q} \right). \quad (7.7)$$

Using the definition of temperature (6.5), the heat function corresponding to the ensemble, the enthalpy is found

$$H_q = \mathcal{M}^{(1-q)N\mathfrak{L}_1} \left(\frac{(\mathfrak{D}_1)^q}{(\Gamma(\mathfrak{D}_1))^{1-q}} \right)^{\mathfrak{L}_1} \left(\frac{1}{P} \right)^{(1-q)N\mathfrak{L}_1} \left(\frac{1}{\beta} \right)^{\mathfrak{L}_1} \quad (7.8)$$

The specific heat at constant pressure evaluated from (7.8) through the use of (6.6) is

$$C_q|_P = (\mathfrak{D}_1)^{q\mathfrak{L}_1} k \mathfrak{L}_1 \left(\frac{\mathcal{M}^N}{\Gamma(\mathfrak{D}_1)} \left(\frac{1}{P} \right)^N \left(\frac{1}{\beta} \right)^{\mathfrak{D}_1} \right)^{(1-q)\mathfrak{L}_1}. \quad (7.9)$$

The average volume calculated using (6.7) can be rewritten to obtain the equation of state given below

$$PV_q = \frac{N}{\beta} \left(\mathcal{M}^N \frac{(\mathfrak{D}_1)^{\mathfrak{D}_1}}{\Gamma(\mathfrak{D}_1)} \left(\frac{1}{P} \right)^N \left(\frac{1}{\beta} \right)^{\mathfrak{D}_1} \right)^{(1-q)\mathfrak{L}_1}. \quad (7.10)$$

The internal energy evaluated through the definition of the expectation value of the observable (6.8) is

$$U_q(\beta) = \frac{DN}{2\beta} \left(\frac{\mathcal{M}^N}{\Gamma(\mathfrak{D}_1 + 1)} \left(\frac{1}{P} \right)^N \left(\frac{1}{\beta} \right)^{\mathfrak{D}_1} \right)^{(1-q)\mathfrak{L}_1}. \quad (7.11)$$

The calculated value of the internal energy has also been checked through a different procedure using the Legendre transformation $H_q = U_q + PV_q$. From (7.11) the specific heat at constant volume found using (6.9) is

$$C_q|_V = \frac{DN}{2} k \mathfrak{L}_1 \left(\frac{\mathcal{M}^N}{\Gamma(\mathfrak{D}_1 + 1)} \left(\frac{1}{P} \right)^N \left(\frac{1}{\beta} \right)^{\mathfrak{D}_1} \right)^{(1-q)\mathfrak{L}_1}. \quad (7.12)$$

Using the results corresponding to the specific heat at constant pressure (7.9) and the specific heat at constant volume (7.12) the q -generalization of the Mayer's relation is obtained

$$C_q|_P - C_q|_V = Nk \mathfrak{L}_1 \left(\frac{\mathcal{M}^N}{\Gamma(\mathfrak{D}_1 + 1)} \left(\frac{1}{P} \right)^N \left(\frac{1}{\beta} \right)^{\mathfrak{D}_1} \right)^{(1-q)\mathfrak{L}_1}. \quad (7.13)$$

The ratio between the specific heat at constant pressure (7.9) and the specific heat at constant volume (7.12)

$$\gamma = \frac{C_q|_P}{C_q|_V} = 1 + \frac{2}{D} \quad (7.14)$$

is interestingly independent of q and N . We have observed the same result in the isothermal-isobaric ensemble (3.21). In the extensive $q \rightarrow 1$ limit the standard Boltzmann-Gibbs results are recovered.

B. Extreme relativistic ideal gas in (N, P, H) ensemble

The extreme relativistic classical ideal gas described by the Hamiltonian (3.23) is studied in the (N, P, H) ensemble. The volume enclosed by the surface of constant enthalpy is given by

$$\Sigma(N, P, H) = \sum_V \frac{1}{N! h^{DN}} \int_{r_i} \int_{p_i} \Theta \left(c \sum_i p_i + PV - H \right) \prod_{i=1}^N d^D r_i d^D p_i. \quad (7.15)$$

In (7.15) the result of the momentum integration is

$${}_{er}\mathcal{I}_p = \int_{c \sum_i^{DN} p_i \leq H - PV} d^{DN} p_i = \frac{1}{\Gamma(DN + 1)} \left(\frac{2\pi^{\frac{D}{2}} \Gamma(D)}{\Gamma(\frac{D}{2})} \right)^N (H - PV)^{DN}. \quad (7.16)$$

The expression (7.16) is substituted in (7.15) and the resulting expression is integrated over the position coordinates. Replacing the summation over the volume eigenstates by an integration to consider the continuum nature of volume and adopting the shell particle method of counting of volume states the final expression for $\Sigma(N, P, H)$ is

$$\Sigma(N, P, H) = \Delta^N \left(\frac{1}{P} \right)^N \frac{H^{\mathfrak{D}_2}}{\Gamma(\mathfrak{D}_2 + 1)}, \quad (7.17)$$

which enables us to calculate the surface of the isoenthalpic curve via the relation (6.3)

$$\Omega(N, P, H) = \Delta^N \left(\frac{1}{P} \right)^N \frac{H^{\mathfrak{D}_2 - 1}}{\Gamma(\mathfrak{D}_2)}. \quad (7.18)$$

The nonextensive entropy (6.4) of the extreme relativistic ideal gas obtained from (7.17) is

$$S_q(N, P, H) = k \left(\frac{\left(\Delta^N \left(\frac{1}{P} \right)^N \frac{H^{\mathfrak{D}_2}}{\Gamma(\mathfrak{D}_2 + 1)} \right)^{1-q} - 1}{1 - q} \right). \quad (7.19)$$

Using the definition of temperature in the isoenthalpic-isobaric ensemble (6.5) in conjunction with the expression for the entropy (7.19) we find the enthalpy

$$H_q = \Delta^{(1-q)N\mathfrak{L}_2} \left(\frac{(\mathfrak{D}_2)^q}{(\Gamma(\mathfrak{D}_2))^{1-q}} \right)^{\mathfrak{L}_2} \left(\frac{1}{P} \right)^{(1-q)N\mathfrak{L}_2} \left(\frac{1}{\beta} \right)^{\mathfrak{L}_2}. \quad (7.20)$$

The specific heat at constant pressure obtained from the enthalpy via (6.6) is

$$C_q|_P = (\mathfrak{D}_2)^{q\mathfrak{L}_2} k \mathfrak{L}_2 \left(\frac{\Delta^N}{\Gamma(\mathfrak{D}_2)} \left(\frac{1}{P} \right)^N \left(\frac{1}{\beta} \right)^{\mathfrak{D}_2} \right)^{(1-q)\mathfrak{L}_2}. \quad (7.21)$$

The computed expression for the average volume using (6.7) is rewritten to give the equation of state

$$PV_q = \frac{N}{\beta} \left(\Delta^N \frac{(\mathfrak{D}_2)^{\mathfrak{D}_2}}{\Gamma(\mathfrak{D}_2)} \left(\frac{1}{P} \right)^N \left(\frac{1}{\beta} \right)^{\mathfrak{D}_2} \right)^{(1-q)\mathfrak{L}_2}. \quad (7.22)$$

Making use of the formula for the expectation value (6.8), the calculated form of the internal energy is

$$U_q(\beta) = \frac{DN}{\beta} \left(\frac{\Delta^N}{\Gamma(\mathfrak{D}_2 + 1)} \left(\frac{1}{P} \right)^N \left(\frac{1}{\beta} \right)^{\mathfrak{D}_2} \right)^{(1-q)\mathfrak{L}_2}, \quad (7.23)$$

and this perfectly agrees with the result found using the Legendre transformation $H = U + PV$. From the internal energy the specific heat at constant volume can be found:

$$C_q|_V = DN k \mathfrak{L}_2 \left(\frac{\Delta^N}{\Gamma(\mathfrak{D}_2 + 1)} \left(\frac{1}{P} \right)^N \left(\frac{1}{\beta} \right)^{\mathfrak{D}_2} \right)^{(1-q)\mathfrak{L}_2}. \quad (7.24)$$

The ratio between the heat capacities at constant pressure and constant volume

$$\gamma = \frac{C_q|_P}{C_q|_V} = 1 + \frac{1}{D}, \quad (7.25)$$

is found to be independent of both the nonextensive parameter and the number of particles N , similar to the result observed in (3.35). The enthalpy, internal energy and the specific heats go to their respective Boltzmann-Gibbs value in the $q \rightarrow 1$ limit.

The thermodynamic quantities corresponding to the Tonks gas (3.36) can also be computed through a procedure identical to the one employed in the case of the nonrelativistic and extreme relativistic classical ideal gas. The results can be easily read from the expressions corresponding to the nonrelativistic gas through the use of the free length $L_{f;q}$ in the place of the volume V and setting the dimension $D = 1$. The equation of state of the Tonks gas thus obtained is

$$PL_{f;q} = \frac{N}{\beta} \mathcal{M}_1^{(1-q)N\mathfrak{L}_{1:1}} \left(\frac{\frac{3N}{2}}{\Gamma(\frac{3N}{2})} \right)^{(1-q)\frac{3N}{2}\mathfrak{L}_{1:1}} \left(\frac{1}{P} \right)^{(1-q)N\mathfrak{L}_{1:1}} \left(\frac{1}{\beta} \right)^{(1-q)\frac{3N}{2}\mathfrak{L}_{1:1}}. \quad (7.26)$$

It can be seen that equation (7.26) recovers its standard Boltzmann-Gibbs result $PL_{f;q} = NkT$ in the $q \rightarrow 1$ limit.

VIII Adiabatic ensemble with number fluctuations

The adiabatic ensemble with number fluctuations was first discussed in detail in [10] in the context of Boltzmann-Gibbs ensemble. This ensemble is the adiabatic counterpart of the grandcanonical ensemble and the Hill energy is the corresponding heat function. Though the integration with respect to the position and the momentum coordinates can be carried easily, it is not possible to carry the sum over all possible values of N . So in this section we give only a formal expression corresponding to the phasespace volume, surface area, the Hill energy and the equation of state.

A. Nonrelativistic Ideal gas

The volume of phasespace enclosed by the curve of constant Hill energy \mathcal{L} after carrying out the integrations over the position and the momentum coordinates is

$$\Sigma(\mu, V, \mathcal{L}) = \sum_{N=0}^{\infty} \frac{V^N}{N! \Gamma\left(\frac{DN}{2} + 1\right)} \mathcal{M}^N (\mathcal{L} + \mu N)^{\frac{DN}{2}}. \quad (8.1)$$

The surface area corresponding to the phasespace curve of constant Hill energy can arrived at through the use of (6.3). The equation of state describing the classical ideal gas in this ensemble is

$$PV_q = \frac{kT}{\Sigma^q} \sum_{N=0}^{\infty} N \frac{V^N}{N! \Gamma\left(\frac{DN}{2} + 1\right)} \mathcal{M}^N (\mathcal{L} + \mu N)^{\frac{DN}{2}}. \quad (8.2)$$

The formal expression for the average number of particles arrived at through the use of (6.7) is

$$N_q = \frac{kT}{\Sigma^q} \sum_{N=0}^{\infty} N \frac{V^N}{N! \Gamma\left(\frac{DN}{2}\right)} \mathcal{M}^N (\mathcal{L} + \mu N)^{\frac{DN}{2}-1}. \quad (8.3)$$

B. Extreme relativistic Ideal gas

For an extreme relativistic classical ideal gas described by the hamiltonian (3.23), the phase space volume calculated is

$$\Sigma(\mu, V, \mathcal{L}) = \sum_{N=0}^{\infty} \frac{V^N}{N! \Gamma(DN + 1)} \Delta^N (\mathcal{L} + \mu N)^{DN}. \quad (8.4)$$

The equation of state and the average number of particles of the extreme relativistic gas corresponding to this adiabatic ensemble are

$$PV_q = \frac{kT}{\Sigma^q} \sum_{N=0}^{\infty} N \frac{V^N}{N! \Gamma(DN)} \Delta^N (\mathcal{L} + \mu N)^{DN}, \quad (8.5)$$

$$N_q = \frac{kT}{\Sigma^q} \sum_{N=0}^{\infty} N \frac{V^N}{N! \Gamma(DN - 1)} \Delta^N (\mathcal{L} + \mu N)^{DN-1}. \quad (8.6)$$

In the $q \rightarrow 1$ the above quantities reduce to the standard Boltzmann-Gibbs equations. Substituting $D = 1$ and replacing the volume by the free length in the thermodynamic expression for the nonrelativistic ideal gas, we can arrive at relations corresponding to the Tonks gas.

IX Adiabatic ensemble with volume and number fluctuations

An adiabatically confined system which can exchange both volume and particles with the bath is described by this ensemble. In the classical Boltzmann-Gibbs case such an ensemble was first described and discussed in detail in [11]. The heat function of the system is the R heat function and this is the adiabatic counterpart of the generalized ensemble. Similar to the previous ensemble, the N summation is difficult to carry and so we present the results as a formal sum.

A. Nonrelativistic Ideal gas

In the ensemble with both volume and number fluctuations, the phasespace volume of the classical nonrelativistic ideal gas enclosed by a curve of constant R is

$$\Sigma(\mu, P, R) = \sum_{N=0}^{\infty} \frac{\mathcal{M}^N}{\Gamma(\mathfrak{D}_1 + 1)} \left(\frac{1}{P} \right)^N (R + \mu N)^{\mathfrak{D}_1}. \quad (9.1)$$

Using the expression for the phase space volume (9.1), the equation of state and the average number of particles is obtained

$$PV_q = \frac{kT}{\Sigma^q} \sum_{N=0}^{\infty} N \frac{\mathcal{M}^N}{\Gamma(\mathfrak{D}_1 + 1)} (R + \mu N)^{\mathfrak{D}_1}, \quad (9.2)$$

$$N_q = \frac{kT}{\Sigma^q} \sum_{N=0}^{\infty} N \frac{\mathcal{M}^N}{\Gamma(\mathfrak{D}_1)} (R + \mu N)^{\mathfrak{D}_1 - 1}. \quad (9.3)$$

B. Extreme relativistic Ideal gas

In the case of an extreme relativistic ideal gas, the phase space volume enclosed by a curve of constant R is

$$\Sigma(\mu, P, R) = \sum_{N=0}^{\infty} \frac{\Delta^N}{\Gamma(\mathfrak{D}_2 + 1)} \left(\frac{1}{P} \right)^N (R + \mu N)^{\mathfrak{D}_2}, \quad (9.4)$$

which leads to the equation of state and the average number of particles given below

$$PV_q = \frac{kT}{\Sigma^q} \sum_{N=0}^{\infty} N \frac{\Delta^N}{\Gamma(\mathfrak{D}_2)} \left(\frac{1}{P} \right)^N (R + \mu N)^{\mathfrak{D}_2}, \quad (9.5)$$

$$N_q = \frac{kT}{\Sigma^q} \sum_{N=0}^{\infty} N \frac{\Delta^N}{\Gamma(\mathfrak{D}_2 - 1)} \left(\frac{1}{P} \right)^N (R + \mu N)^{\mathfrak{D}_2 - 1}. \quad (9.6)$$

The $q \rightarrow 1$ limit is respected in all the above mentioned cases. The thermodynamic expressions corresponding to the Tonks gas can be arrived directly from the relations given for the nonrelativistic gas by substituting $D = 1$ and replacing volume by the free length.

The summation over the number of particles could not be evaluated in both the ensemble with the number fluctuations and the ensemble with number and volume fluctuations. But the thermodynamic quantities in both these ensembles may be obtained through the use of a molecular dynamics simulation.

X Remarks

A comprehensive investigation on the different kinds of ensembles has been carried out in the present work. We notice that there are two different classes of ensembles namely the isothermal class and the adiabatic class. The thermal equilibration in the isothermal class happens with respect to the temperature. Isothermal class comprises of the canonical ensemble, the isothermal-isobaric ensemble, the grandcanonical ensemble and the generalized ensemble. We notice that the thermodynamic relations corresponding to these four ensembles can be presented through a unified formulation. Such a formulation is evolved for both the second and the third constraint formalisms though the latter is the currently accepted formulation of nonextensive q -statistical mechanics. The development of unified formulation corresponding to the second constraint has been done with a view to apply nonextensive q statistics in computational simulations like Montecarlo and molecular dynamics. It is a well known fact that the probabilities in the third constraint are implicit quantities. In calculational procedures involving simulations it is easier to find the thermodynamic quantities in the second constraint and later transform them to the third constraint. Towards this end a generalization of the temperature dependent interrelation between the second and the third constraint introduced in Ref. [16] has been accomplished.

The unified formulation developed is applied to study the isothermal-isobaric, grand-canonical, and the generalized ensembles through specific examples viz the classical non-relativistic, and, extreme relativistic ideal gas models. Since the canonical ensemble has already been studied in detail in Ref. [15,16] it has not been considered in our present work. In the isothermal-isobaric ensemble, the implicit equations corresponding to the generalized partition function and the enthalpy are solved to obtain their corresponding explicit expressions. From these quantities the average volume, the internal energy, the specific heat at constant pressure, and, the specific heat at constant volume are obtained. All the above mentioned thermodynamic quantities are obtained as exact results. The specific heats were dependent on the nonextensivity parameter q and the temperature in both the models. Interestingly we notice that the ratio between the specific heat at constant pressure and the specific heat at constant volume is independent of both q and N . A similar exact computation of the gas models in the grandcanonical and the generalized ensembles were found to be difficult. So, we employed a perturbative procedure developed in [18,23] based on the disentangling of q -exponential [22]. The perturbative series corresponding to the generalized partition function, the sum of q -weights and the

heat function are obtained up to a predetermined order in the third constraint formalism. The determined implicit quantities are then solved recursively to obtain the final explicit forms which are used to find the thermodynamic results. The fact that these quantities are uncoupled and exactly solvable in the $q = 1$ limit facilitates the recursive procedure. In the grandcanonical ensemble, the final results are computed up to second order in the expansion variable $(1 - q)$ whereas in the generalized ensemble the results are displayed only up to the first order. Though the results have been calculated and displayed only up to a particular order in the expansion parameter, the procedure can be extended to any arbitrary order in $(1 - q)$.

A similar unification procedure is used to create a generalized formulation for the adiabatic ensembles. The microcanonical ensemble, the isoenthalpic-isobaric ensemble, the adiabatic ensemble with number fluctuations, and the adiabatic ensemble with number and volume fluctuations belong to this class. The nonextensive q generalization of the equipartition theorem and the virial theorem have been obtained in a unified sense. The (N, P, H) ensemble, (μ, V, L) ensemble and the (μ, P, R) ensemble have been studied through the examples of classical nonrelativistic ideal gas and the extreme relativistic ideal gas. The above mentioned ideal gas models have been solved in the isoenthalpic-isobaric ensemble. The exact expression corresponding to the entropy, the enthalpy, the internal energy and the heat capacities at both constant pressure and at constant volume were found. In the case of (μ, V, L) and the (μ, P, R) ensemble an exact solution could not be arrived and so the thermodynamic quantities have been expressed as formal sums. An interesting observation is made from the study of the ideal gas models in the various ensembles. The gas models were exactly solvable in the isothermal-isobaric and the isoenthalpic-isobaric ensembles. In both these ensembles we notice that the ratio of the specific heat at constant pressure and the specific heat at constant volume was found to be independent of the nonextensivity parameter q , the number of particles N and the temperature. This is despite the fact that the individual heat capacities were dependent on these three factors. Meanwhile the difference between the heat capacities was found to be dependent on these three factors.

The choice of an ensemble to study a problem in statistical mechanics depends on the physical situation. The microcanonical ensemble is used to study completely isolated systems, whereas the canonical ensemble is used to study closed systems which exchange energy with the surroundings. The grandcanonical ensemble is used to study systems capable of exchanging particles with its surroundings. A system like colloidal particles or macromolecules immersed in a solvent experiences a constant pressure and so they can be suitably studied using the isothermal-isobaric ensembles. Depending on whether a fluid under constant pressure is isothermally or adiabatically confined, we can use the isothermal-isobaric or the isoenthalpic-isobaric ensemble. The generalized ensemble can be used to analyze systems whose size varies while the pressure is maintained constant. Typical examples include molecular clusters in a one component gas and a system of bound ions or molecules on a protein molecule. Also there are situations in nature where an external electric field, magnetic field or gravitational field acts on a thermodynamic system. The construction of a class of ensembles comprising of an external field along with the thermal, mechanical and chemical variables, and their consequent application to study problems like rotating black holes and charged polymers like DNA molecules should

be worth pursuing.

The unification procedure developed in the current work for the nonextensive q -entropy (1.1) can be extended to other kinds of nonextensive entropies like κ entropy [28] and the two parameter entropies [29,30]. Such an effort will help us to understand the change in the structure of thermostatistics due to nonextensivity. It has been noticed in Ref. [10] that there is an inherent pairing between the isothermal and the adiabatic ensembles that is each isothermal ensemble has an adiabatic counterpart. These pairs can be identified through the fact that they have the same heat function. An interrelation between the isothermal and adiabatic ensemble can be established through a Laplace transformation. The canonical ensemble and the microcanonical ensemble have been interrelated in the nonextensive q -statistics through a q -generalization of the Laplace transform [31]. Currently we are working on developing a unified formulation of the q -Laplace transform to connect any of the isothermal ensemble to its adiabatic counterpart. The results will appear elsewhere.

Acknowledgements

The authors would like to thank Professor Ranabir Chakrabarti for helpful discussions and motivation, and Dr. Niyaz Ahamed Mandir for providing crucial references. R. Chandrashekar would like to acknowledge the fellowship received from Council of Scientific and Industrial Research (India).

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